THERMALLY REARRANGED POLYMERIC MEMBRANE FOR NATURAL GAS SEPARATION

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MECHANICAL ENGINEERING

December 2016

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BY

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A Thesis Presented to the
DEANSHIP OF GRADUATE STUDIES

KING FAHD UNIVERSITY OF PETROLEUM & MINERALS

DHAHRAN, SAUDI ARABIA

In Partial Fulfillment of the
Requirements for the Degree of

MASTER OF SCIENCE

In

MECHANICAL ENGINEERING

December 2016

KING FAHD UNIVERSITY OF PETROLEUM & MINERALS

DHAHRAN- 31261, SAUDI ARABIA

DEANSHIP OF GRADUATE STUDIES

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MASTER OF SCIENCE IN MECHANICAL ENGINEERING

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2016

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ACKNOWLEDGMENTS

First and foremost, I would like to express my sincere gratitude to Allah for providing me with strength and patience to complete this degree.

Also, I would like to thank my advisor Dr. Khaled Mezghani for his great support and guidance throughout my thesis work.

I would like to acknowledge the funding received from King Abdulaziz City for Science and Technology (KACST) through the Technology and Innovation Center (TIC) on Carbon Capture and Sequestration, project number TIC-CCS-5. Also, acknowledgment is due to the support provided by KACST through project # AR-32-11. Furthermore, the support from King Fahd University of Petroleum and Minerals (KFUPM) for the completion of this work is also appreciated.

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LIST OF ABBREVIATIONS

CA	:	Cellulose Acetate
CH_4	:	Methane
CMS	:	Carbon Molecular Sieve
CO_2	:	Carbon Dioxide
C2+	:	Heavy Hydrocarbons
DAB	:	3,3′-Diaminobenzidine
FTIR	:	Fourier Transform Infra-Red
GC	:	Gas Chromatography
He	:	Helium
H_2	:	Hydrogen
H_2S	:	Hydrogen Sulfide
MFC	:	Mass Flow Controller
MFM	:	Mass Flow Meter
MMM	:	Mixed Matrix Membranes
N_2	:	Nitrogen
O_2	:	Oxygen

P	:	Permeability
PAAc	:	Poly(Amino Amic Acid)
PAI	:	Polyaminoimide
PBI	:	Polybenzimidazole
PBO	:	Polybenzoxazoles
PBZ	:	Polybenzothiazoles
PES	:	Polysolfune
PIMs	:	Polymer of Intrinsic Microporosity
PPL	:	Polypyrrolone
PPO	:	Poly Phenylene Oxide
PT	:	Pressure Transducer
SCCM	:	Standard Cubic Centimeter Per Minute
SEM	:	Scanning Electron Microscope
STP	:	Standard Temperature Pressure
TR	:	Thermally Rearranged
6FDA	:	4 4'-(Hexafluoroisopropylidene) Diphthalic Anhydride

ABSTRACT

Full Name : Mohammad Saad AlQahtani

Thesis Title : Thermally Rearranged Polymeric Membrane for Natural Gas Separation

Major Field : Materials Science

Date of Degree : December 2016

Natural gas processing is one of the large industries in the world, by processing around 3 trillion standard cubic meter per year. In natural gas processing, contaminations like carbon dioxide must be removed to reach a saleable quality. Polymeric membrane has been investigated for that purpose as it has many advantages over the conventional amine technology. In this study, thermally rearranged (TR) polymer is considered as a potential material for the gas separation membrane due to its outstanding performance and chemical resistivity. The gas permeation properties for both pure and mixed gases for thermally rearranged polypyrrolone (PPL-450) membranes have been studied which were synthesized from 6FDA and DAB. PPL-450 membrane has shown high permeability and excellent selectivity for CO_2 and Helium over CH_4. Although, CO_2 permeability (as well as all other gases) has dropped in case of mixed gas feed condition, the selectivity of CO_2/CH_4 has increased. Furthermore, at high pressure (800 psig) with about 10% stage cut, PPL membrane was able to remove 80% of the carbon dioxide in the feed. Likewise, Helium has been recovered from very dilute concentration of 0.14% with more than 80% recovery at 5% stage cut. In addition, the membrane has demonstrated an outstanding resistivity to CO_2 plasticization at high pressures.

ملخص الرسالة

الاسم الكامل: محمد سعد القحطاني

عنوان الرسالة: غشاء البوليمر المعالج حراريا لفصل وتنقية الغاز الطبيعي

التخصص: علم المواد – هندسة ميكانيكية

تاريخ الدرجة العلمية: ديسمبر ٢٠١٦

معالجة الغاز الطبيعي هي واحدة من الصناعات الكبيرة في العالم من خلال معالجة حوالي ٣ تريليون متر مكعب سنويا. الغاز الطبيعي يحتوي على العديد من الشوائب مثل غاز ثاني أوكسيد الكربون ويجب ازالتها للوصول لجودة قابلة للبيع. تقنية الفصل باستخدام الاغشية لها العديد من المزايا بالمقارنة مع التقنيات التقليدية. هذه الدراسة تركز على الأغشية المعالجة حراريا نظرا لأدائها المميز في عملية الفصل ومقاومتها للمواد الكيميائية. لكن لا تزال هذه التقنية بعيد عن الاستخدام الصناعي للنقص الواضح في البيانات والبحوث المتعلقة بها. خصوصا الدراسات باستخدام خليط من الغازات وليس فقط غاز واحد. ركزت هذه الدراسة على دراسة تأثير استخدام عدة أنواع من خليط الغازات (ثنائي، ثلاثي ورباعي) لاستهداف تطبيق معين محتمل في صناعة الغاز الطبيعي مثل إزالة ثاني أكسيد الكربون واستخلاص الهيليوم. الغشاء المستخدم في هذه الدراسة أظهر نفاذية عالية لثاني أكسيد الكربون وانتقائية عالية بالمقارنة مع المثان بالرغم من الضغط العالي (٨٠٠ رطل لكل بوصة مربعة). الغشاء كان قادر على إزالة ٨٠٪ من ثاني أكسيد الكربون واستخلاص أكثر من ٨٠٪ من الهليوم. كما أظهر الغشاء مقاومة عالية لثاني أكسيد الكربون تحت ضغط عالي.

CHAPTER 1

INTRODUCTION

The demand for the energy is increasing every day due to the rise in the world population. Energy sources like oil and coal have great impact on the environment. On the other hand, natural gas is clean and more efficient energy source than other conventional energy sources [1, 2]. At worldwide level, the total natural gas consumption is about 3 trillion standers cubic meter per year. Natural gas, as extracted from the well, is mainly composed of Methane (70% - 90%), Ethane, Propane and higher hydrocarbons. Moreover, the gas contains carbon dioxide, nitrogen, water and hydrogen sulfide, which are considered as impurities. The gas composition varies from well to well (Table 1) Also, each region has its own specification for natural gas delivery and US specification is shown in Table 1. Therefore, natural gas has to be treated before using it as an energy source, and that makes a big market for the gas separation processes and equipment [1].

Table 1 Natural gas well & pipeline specifications and composition* [2]

Gas	Well Composition	Specification
CH_4	70 – 90%	> 97%
CO_2	1 – 10 %	< 2%
N_2	1 – 5 %	< 4%
H_2S	0 – 5 %	< 4 ppm
C2	1.5 – 8 %	< 1%
C3 +	1 – 5 %	-

*based on USA specification.

The current technology used for treating the natural gas is the absorption process. Although, it is the most common used technology for gas separation, it is a costly way to purify the natural gas. Figure 1 shows a typical absorption process, there are two columns, first column is for handling high pressure and the second one is operating at low pressure. The natural gas enters the bottom of the column and the absorbent liquid flows from the top. Then, the liquid absorbs the contamination (CO_2, water or heavy hydrocarbons) from the gas and goes to the second column, which is a stripper column. In the stripper column, the absorbent liquid will be heated at low pressure to get rid of the impurities. Finally, the clean absorbent liquid is recycled to the first column. The type of the absorbent liquid depends on which component to be removed. Amine absorbents are the most common used type for removing carbon dioxide, and for water removal triethylene glycol is used. In case of heavy hydrocarbon removal, lean oil is used. This absorber-stripper treatment process required a lot of energy, large footprint and a serious maintenance issue due to corrosion.

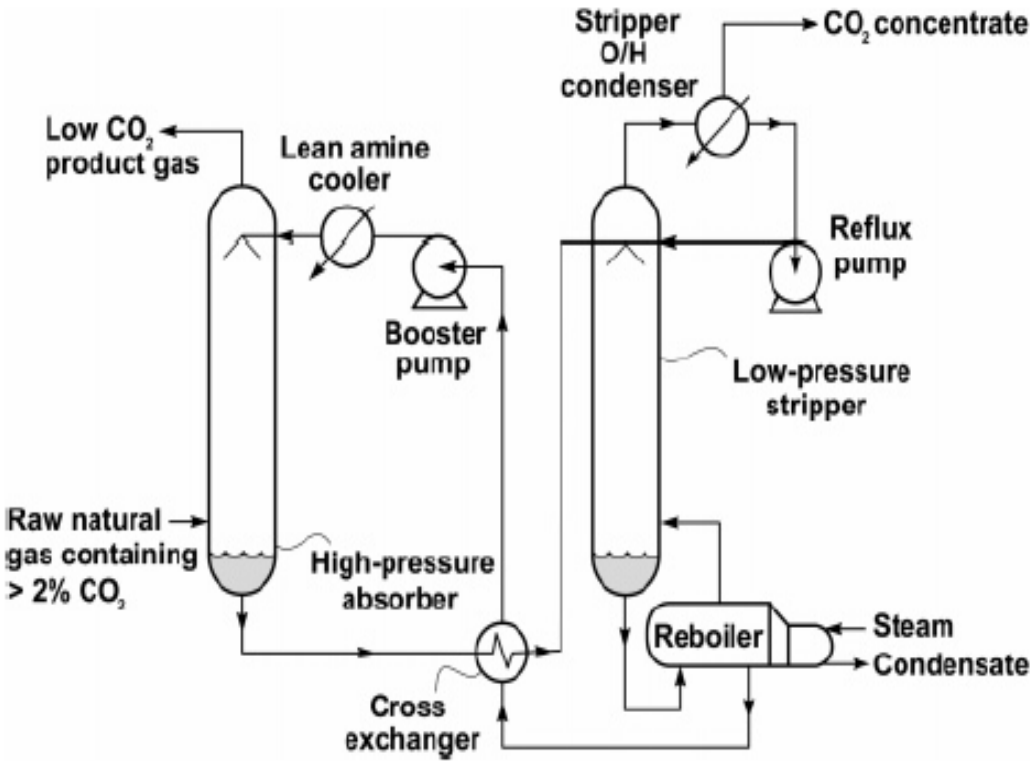


Figure 1 Typical NG absorption process using Amine absorbent to remove CO_2. [2]

Membrane gas separation has many advantages over the conventional ways such as cryogenic distillation, absorption and adsorption processes. Energy conservation is one of the main advantages of using membrane technology because it does not require a phase change. Moreover, the small footprint makes this technology preferable in remote areas and off shores. Also, the fact that the membranes do not have any moving part makes them even better because they need less maintenance. The membrane lifetime and reliability are the main concerns. In addition, membrane is not recommended for high flow rate. Taking CO_2 removal as an example, generally high concentration and low flow rate favors membrane process. In contrast, amine is favor in case of high flow rate with low concentration and hyper system can be use in between those cases as shown in Fig.2. Notice that the location of the plant is not included in those rules and that can change the result [2].

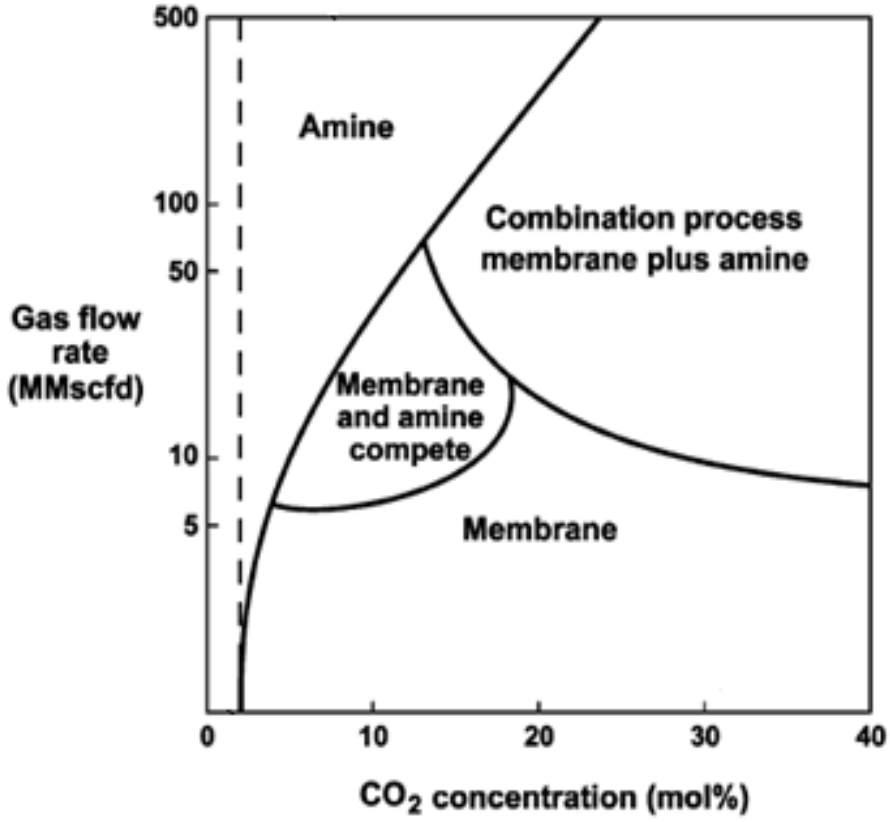


Figure 2 The effect of gas flow rate and CO_2 concentration in the gas on the choice of the technology. [2]

The performance of the membrane depends upon two parameters which are the selectivity and permeability. Where the selectivity is the measure of the separation quality and the permeability is the productivity of the membrane. One limitation of the membrane technology is that there is a tradeoff between the permeability and the selectivity, as one increases the other decreases. It is necessary for polymer membranes to achieve both high permeability and selectivity [6]. Thermally rearrange (TR) membrane is one of few membrane types that overcome this challenge, as shown in figure 3. TR polymers show excellent performance especially for CO_2 removal form natural gas when compared to perfluoropolymers, polyimides, ionic liquid membranes and PIMs.

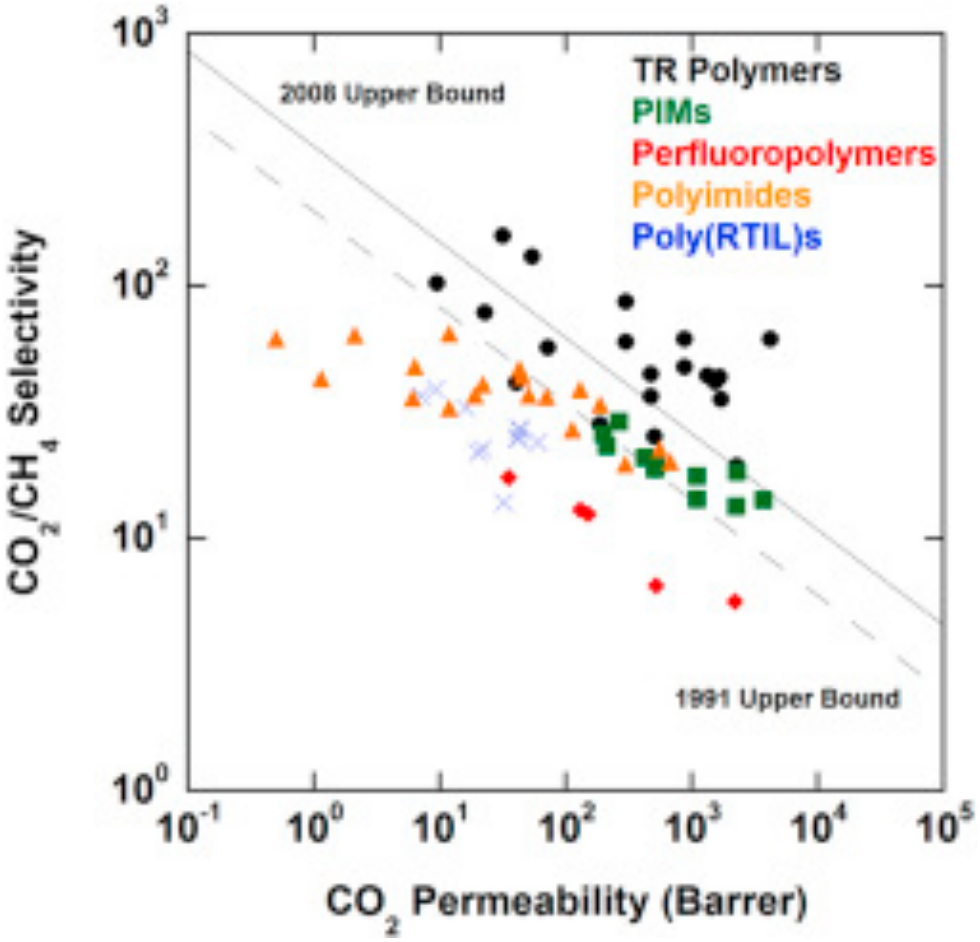


Figure 3 Comparison between TR polymer, PIMs, Polyimides and Poly(RTIL)s . [6]

1.1 Membrane for Natural Gas Separation

1.1.1 History

The membrane technology was known from long time in the mid of 1960s. However, the challenge was in how to fabricate the membrane for industrial uses to be economically feasible. In 1980, several companies were able to launch membrane modules for large production. The first industrial application for gas separation membrane was for hydrogen separation and it was produced by Permea which is now part of Air Product [3]. Moreover, other companies like Separek (UOP now), Cynara (Natco now) and GMS (Kvaerner now) started to make membranes for CO_2 removal from natural gas using cellulose acetate. In the past 20 years, the membranes for gas natural gas separation have grown to become an active area for study and research. New types of membranes were discovered by companies (Table 2) like MTR which manufacture perfluoropolymers and silicone rubber membranes [2, 3].

Table 2 Suppliers of Membrane Natural Gas Separation Systems. [2]

Company	Gas separated	Module type	Membrane material
Medal (Air Liquide)	CO_2	Hollow fiber	Polyimide
W.R. Grace	CO_2	Spiral-wound	Cellulose acetate
Separex (UOP)	CO_2	Spiral-wound	Cellulose acetate
Cynara (Natco)	CO_2	Hollow fiber	Cellulose acetate
ABB/MTR	CO_2, N_2, C3+ hydrocarbons	Spiral-wound	Perfluoro-polymers, Silicone rubber

1.1.2 Theory and Terminology

The membrane performance depends on two main parameters which are the permeability and selectivity. The permeability can be defined as the membrane ability to transport gas through, while the selectivity is the ability of the membrane to separate two gases.

The permeability hinge on both the gas solubility and diffusivity through the membrane and that is what the solution-diffusion model states [3]. Simply, the model says the permeability, P_i, can be written as following:

$$P_i = D_i S_i \quad (1)$$

Where D_i is diffusion coefficient and S_i is the solubility coefficient.

Many factors influence the diffusion coefficient like the penetrant size, free volume and the flexibility of the polymer chain. Larger gas molecules tend to interact more with the polymer material which led to a decrease in the diffusion coefficient. On the other hand, solubility depends on gas condensability which can be representing by the boiling point of the gas. As the boiling point increase, the condensability increase and as a result the solubility coefficient increase as well. The ratio between the gas concentration inside the polymer, C, to the pressure of the gas, p, is basically the solubility coefficient:

$$S_i = \frac{C}{p} \quad (2)$$

The sorption of light gases (e.g. He, H_2, N_2, and CH_4) obey Henry's Law:

$$C_D = k_D p \quad (3)$$

Where k_D is the Henry's Law coefficient. In this case, as the pressure increases the solubility will stay constant. The concentration of molecules absorbed in the polymer matrix, C_D is described by Hennry's law.

Whereas, the concentration of molecules absorbed into micro-cavities, C_H, can be described by langmuir equation:

$$C_H = \frac{C'_H b\, p}{1 + b\, p} \quad (4)$$

where C'_H is the hole saturation constant and b is the hole affinity constant

The combination of the two concepts give the rise to what is called dual mode sorption which describes the sorption of gas molecules into a glassy membrane [4]. The adsorption of gas molecules is assumed to be categorized into two categories;

1. Adsorption of molecules directly into the polymer matrix, C_D.
2. Adsorption of molecules into micro-cavities within the polymer matrix, C_H.

Now, the total concentration of absorbed molecules (Dual-Mode Sorption Model) can be described by the following equation:

$$C = k_D p + \frac{C'_H b\, p}{1 + b\, p} \tag{5}$$

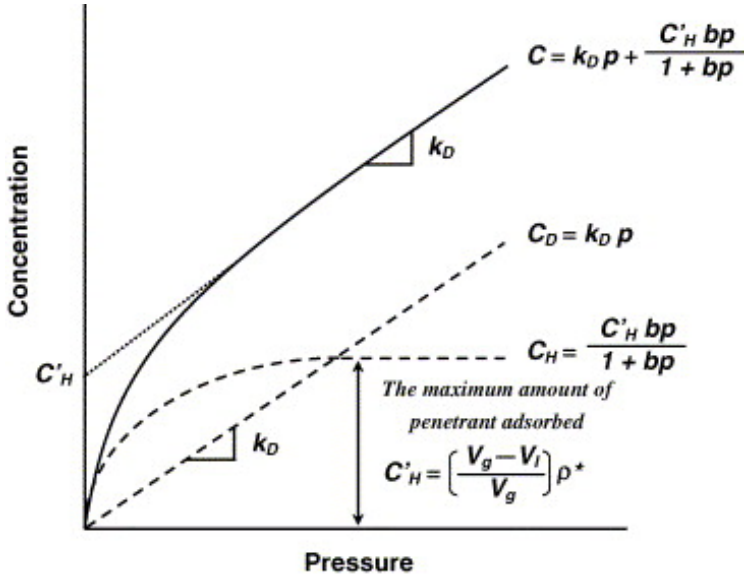


Figure 4 An illustration of the two components that contribute to gas sorption in a glassy polymer according to the dual sorption model. [4]

In the solution diffusion model, the permeability in polymeric membrane for a pure gas is calculated by the following equation [3]:

$$P_i = \frac{Q_i l}{A\,(p_2 - p_1)} \tag{6}$$

Where Q_i is the flow rate of the gas, l is the membrane thickness, A is the membrane area, p_2 is the upstream pressure and p_1 is the downstream pressure.

1.2 Challenges & Limitation

1.2.1 Permeability / Selectivity Trade-off

Getting a membrane with both high permeability and selectivity is the dream of every researcher. Unfortunately, this desired membrane is very difficult to achieve because the flux is proportional to the separation factor. The polymer structures and the chain packing will directly impact membrane's performance. Generally, if the polymer has a tight and rigid structure that will result in a very selective membrane. On the other hand, the flux will be low because the free volume is small in that case. Many studies have dealt with this trade-off relationship and found an upper bound relationship between the permeability and the selectivity. There are different upper bound relationships for different gas pairs (CO_2, N_2, CH_4, He, H_2 and O_2) and Fig. 5 shows and example of CO_2/CH_4 pair. The upper bound line can be expressed by the following:

$$P_i = k\alpha_{ij}^{\,n} \tag{7}$$

Where P_i is the permeability of the more permeable gas, k is a constant, α_{ij} is the selectivity of the two gases and n is the slope of the upper bound line.

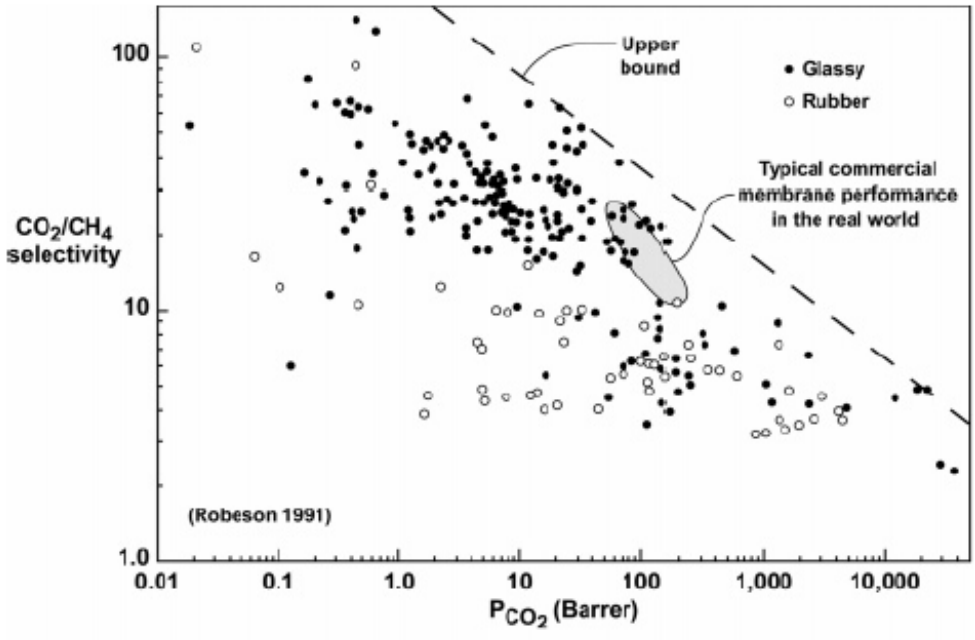


Figure 5 Permeability and selectivity CO_2/CH_4 trade-off. [2]

1.2.2 Plasticization

Plasticization is a phenomenon that is directly related to the capacity of the polymer to sorb (adsorb) penetrant molecules. Acid gases and heavy hydrocarbons, which are easier to condense, tend to adsorb more than less condensable gases, see Fig. 6.

Plasticization occurs to all polymers to different extent, depending on that polymer-gas penetrant interaction. In essence, gas penetrants will adsorb inside the membrane matrix in free volume (no or less selective) and surrounding polymer pendants/groups sights (more selective).

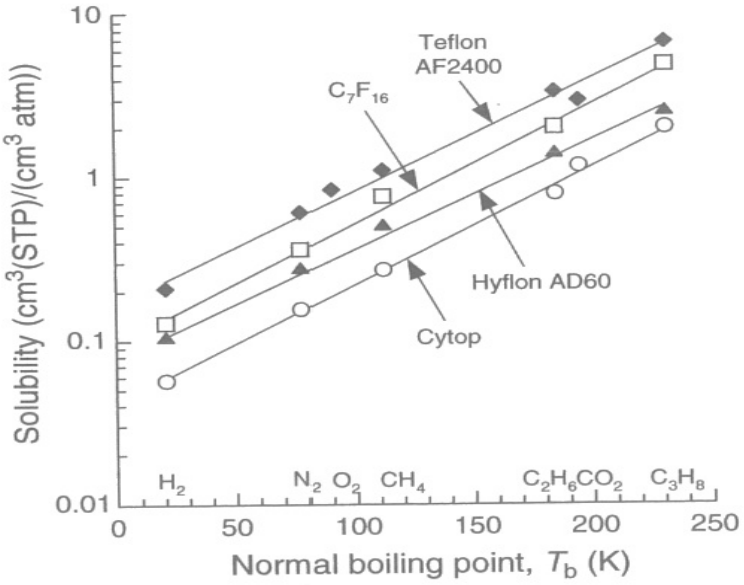


Figure 6 Gas solubility in perfluoroheptane, Teflon, Hyflon and Cytop as a function of penetrants boiling point. [3]

Although plasticization is well noted, however it is a phenomenon that is not yet well understood. The general understanding of plasticization is:

1. It occurs in glassy polymeric membranes (rubbery membranes are already in plasticized state).
2. There is a threshold for the onset of the plasticization that is dependent on:
    a. Membrane chemistry.
    b. Gas penetrants.
    c. Selective layer thickness; thinner morphologies plasticize more readily.

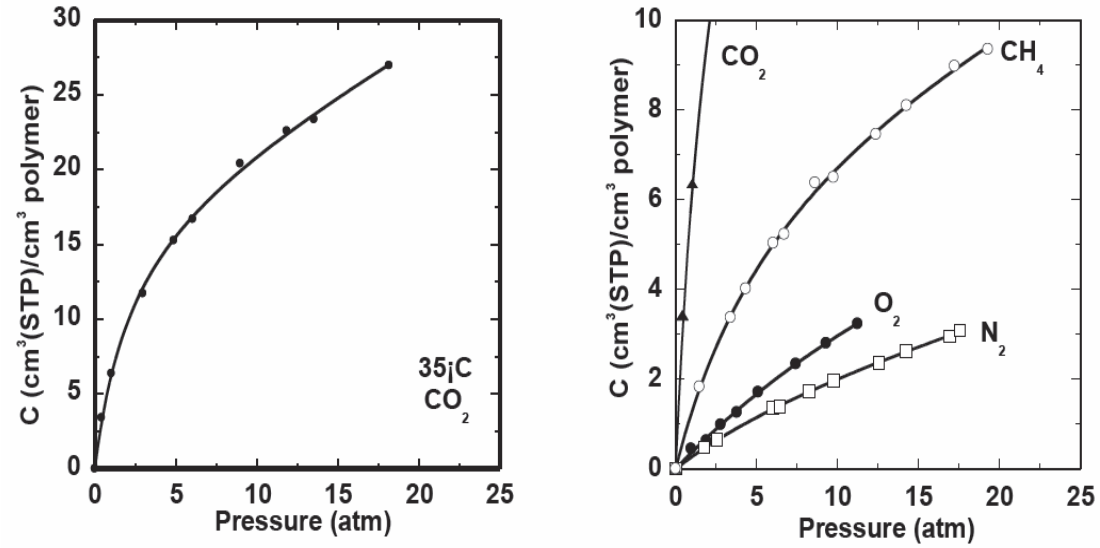


Figure 7 Effect of pressure on different gases in a glassy polymer, Polysulfone. [3]

Plasticization usually affects the membrane performance negatively as it will result in losing its selectivity. This phenomenon can be noticed from the difference between the selectivity at low and high pressure for the pure gases especially for more condensable gases. Basically, as the pressure increases, the polymer matrix adsorbs more gas molecules and at some point, that will swill and open up the membrane structure resulting in higher permeability and lower selectivity.

In the nature gas, carbon dioxide is the main reason of membrane plasticization because of its high condensability comparing to other gases which can be represented by its boiling point. At high pressure, the membrane absorbs large amount of CO_2, it reaches high concentrations in some cases up to 45 cm^3 (STP)/cm^3 polymer. Consequently, the glass transition temperature of the polymer will drop down and the motion of polymer chains will increase. Therefore, the diffusivity of CO_2 inside the polymer increases and that leads to an increase in permeability. Figure 8 shows a comparison of the plasticization effect in three different polymers: PPO, Matrimid and CA. those membranes were expose to 80% CO_2 – 20% CH_4 gas mixture, then the feed pressure was increased gradually [5]. Both Matrimid and CA showed a clear sing of plasticization as the CO_2 permeability went up and CO_2/CH_4 dropped down significantly as the CO_2 fugacity rises. On the other hand, PPO membrane showed a very good resistivity and maintained its performance (permeability and selectivity) as the fugacity increases [5].

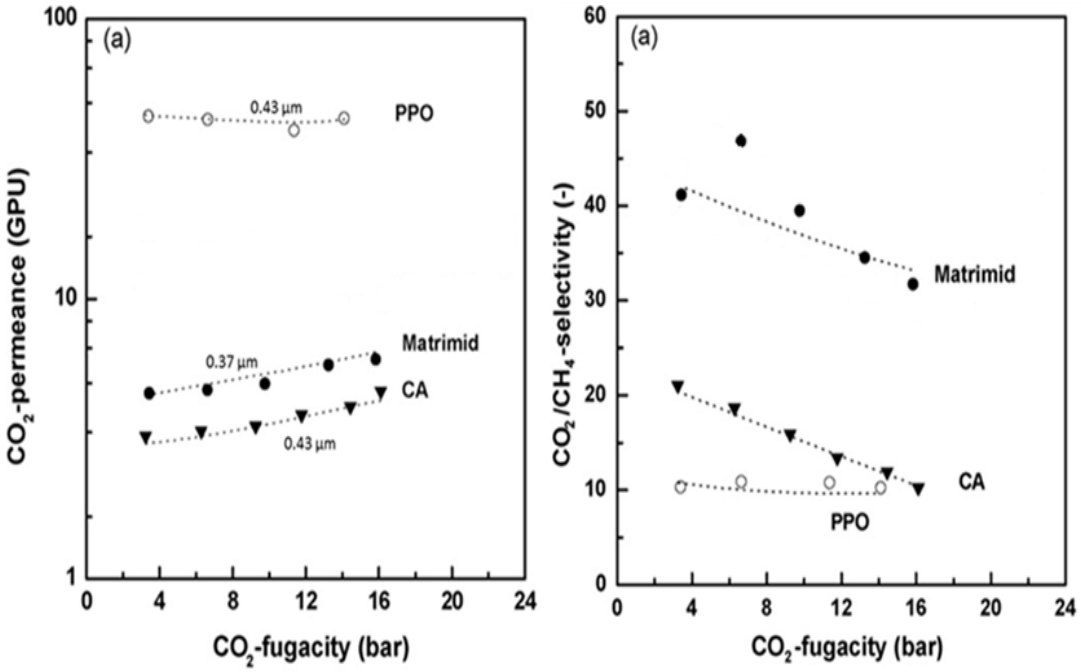


Figure 8 Comparison of CA, Matrimid & PPO hollow fibers to separate (80% CO_2 – 20% CH_4). [5]

1.2.3 Physical Aging & Life Time

Another challenge that affects the reliability of the membrane in industry is physical aging. This usually happens in glass membranes rather than rubbery membranes and the reason for that is because glassy polymers are thermodynamically non-equilibrium material. Unlike the rubbery polymers, glass polymers have excess free volume and that makes them unstable. Physical aging reduces membrane productivity along with other physical properties. It is time dependent; it will decrease with time due to the decrease in the driving force. Moreover, the thickness of the membrane plays a role in controlling the physical aging of the membrane. Higher membrane thickness means less effect on the performance but this will backfire on the membrane's productivity [7]. Figure 9 shows huge drop of CO_2 permeability after the exposure of 220 nm Matrimid membrane for 20 h comparing to 20 µm membrane thicknesses at 32.4 bar.

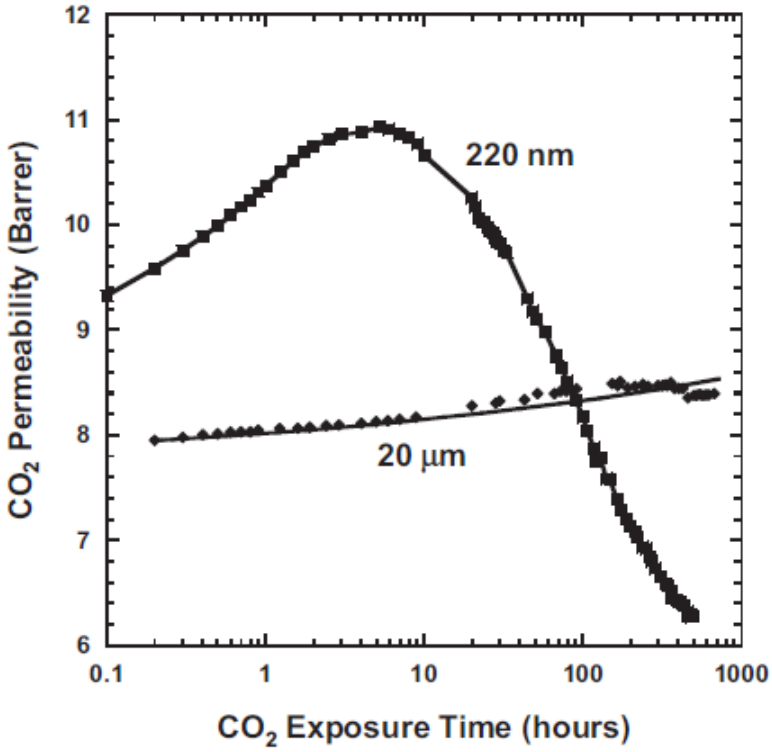
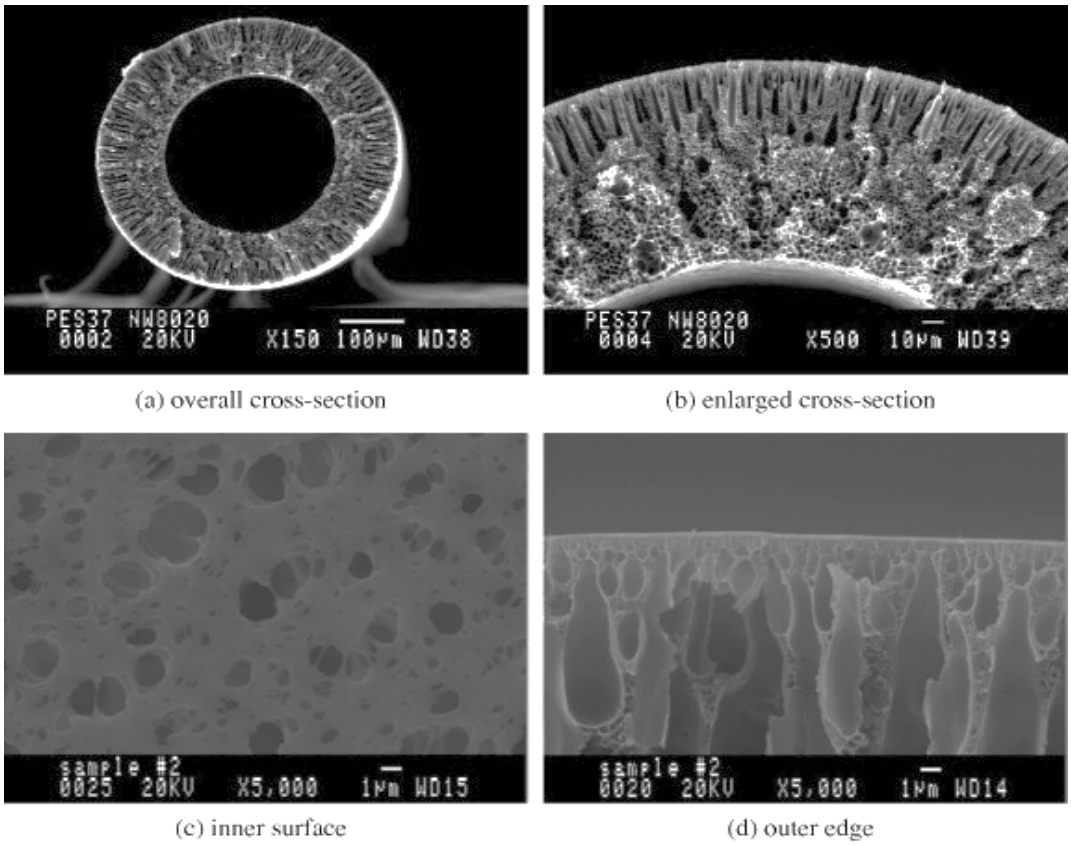


Figure 9 Physical aging in 200 nm and 20 µm Matrimid membranes at 32.4 bar of CO_2. [7]

1.2.4 Other Challenges

There are other challenges that are facing the gas separation membrane growth. Scalability for example is a difficulty that required more attention as many membrane materials showed promising result in lab scale and dense film experiment, however, they failed at bigger scale. In large scales, polymeric membranes have to manufacture in hollow fiber or spiral wound modules and that involves a lot of science and art. In those modules, the membrane is costed on to of porous support, so the selective layer usually has very thin thickness in the range of nm to couple of micrometers. Having such a thin selective layer minimize the membrane material being used which is usually expensive, furthermore, the porous support provides the mechanical strength needed to handle high pressure difference across the membrane. Figure 10 shows cross section SEM images of PES hollow fiber membranes used for industrial gas separation membrane applications [59].



(a) overall cross-section (b) enlarged cross-section

(c) inner surface (d) outer edge

Figure 10 SEM images of developed PES hollow fiber membrane. [59]

1.3 Commercial Membrane for Natural Gas Purification

1.3.1 Cellulose Acetates

Cellulose acetate is one of the first commercial membranes for natural gas separation even though it was used primarily for water desalination. In gas separation, CA is mainly targeting acid gases removal from natural gas. The reason for that is because it has a good CO_2/CH_4 selectivity, above 30 which led to a wide use in industry. One more advantage is the cost of CA membranes, it's relatively low. On the other hand, plasticization is a limitation in this type of membrane which depends on feed pressure and time of exposure as well. Moreover, the CA membrane will not go back to its original performance after the swilling. For example, if the feed pressure get tripled for 5 day only and bring it back to the initial pressure, the selectivity will decrease by more than 30% as shown in Table 3 [9].

CA is synthesized by acetylation of cellulose which is basically replacing the hydroxyl groups on cellulose with acetyl group (figure 11). The degree of acetylation is a key factor that affects the CO_2 permeability dramatically as shown in Fig. 12 [10]. As other many membranes, the performance of CA membranes changes under mixed gas condition due to the competition of all gases to permeate faster. Moreover, the presence of impurities like water and acetone can damage the membrane and even dissolve it. So, a proper pre-treatment is required in that case. A lot of work was done trying to improve CA performance like forming composites with poly (methyl methyacrylate) or poly (ethylene glycol). However, until now there is no real breakthrough happened.

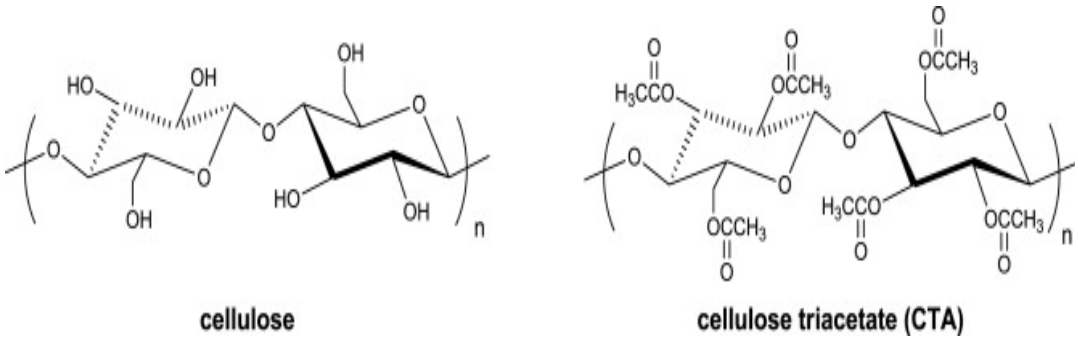


Figure 11 Chemical structure of CA. [6]

Table 3 CO_2 permeability and CO_2/CH_4 selectivity results for a cellulose acetate membrane with a degree of acetylation of 2.45. [9]

	CO_2 permeability (Barrer)	CH_4 permeability (Barrer)	α_{CO_2/CH_4}
Original condition[1]	3.04	0.079	38.0
After exposure[2]	4.57	0.180	25.4

[1] Pure gas at 10 atm.

[2] after exposure to CO_2 at 27.2 atm for 5 days.

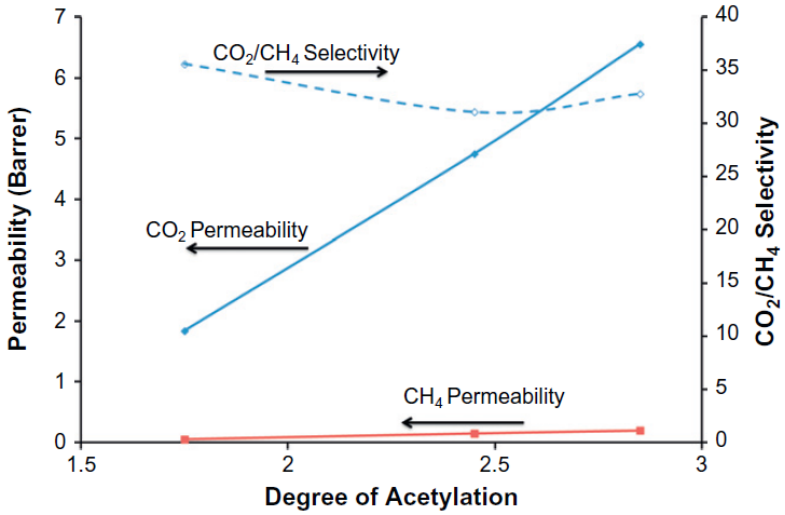


Figure 12 Degree of acetylation effect on membrane permeability and CO_2/CH_4 selectivity, at 35 ^oC and 1 atm. [10]

1.3.2 Polyimide

Polyimides are very well known family of polymer. They have an excellent CO_2/CH_4 selectivity with good permeability and this is explained why there are a lot of studies dealing with this type of polymer. Moreover, polyimides possess a good thermal and chemical resistivity and they are easy to prepare. Also, some PIs have an advantage over the Cellulose Acetates which is the excellent resistivity against plasticization especially cross-linked membranes. There is a wide range of polyimides mostly derived from 6FDA, its structure is shown in figure 13. Table 4 shows some of the polyimide membranes with their performance.

Table 4 Common polyimide membrane performance.

Polymer	CO_2 Permeability (Barrer)	CH_4 Permeability (Barrer)	α (CO_2/CH_4)	Pressure (psi)	Temp. (^oC)	Ref.
Matrimid 5218	6.5	0.19	34	150	35	[6]
6FDA-Durene	458	28.4	16.1	150	35	[11]
6FDA-1,5-NDA	22.6	0.46	49	150	35	[12]
6FDA-TAPOB	7.4	0.098	75	15	25	[13]
6FDA-DATPA	23	0.68	34	150	35	[14]
6FDA-6FpDA	63.9	1.5	39.9	150	35	[15]

6FDA-6FmDA	5.1	0.08	63.8	150	35	[15]
ODPA-TAPOB	0.63	0.0064	98	15	25	[16]
PMDA-TAPOB	3.3	0.66	50	15	25	[16]
DAD-6FDA	381	15.24	25	300	25	[15]
DAM-6FDA	691	48.7	14.2	300	25	[15]
DDBT-BPDA	8.2	0.24	34.3	150	50	[15]

The most common polyimide is Matrimid®. By comparing the commercial polymer with respect to their CO_2 permeability and CO_2/CH_4 selectivity, Matrimid® will be the best polymer. However, under high pressure and acid gas concentration, Matrimid® will plasticize like cellulose acetate. One solution to that problem is to cross-link it, but that might reduce the permeability. The membrane performance is directly related to the chemical structure of the polyimide itself. The tuning of the diamine and dianhydridecan enhance the transport properties. Another way to improve the separation is to make a copolymer from two preferable homo-polymers in order to get optimum value of both permeability and selectivity.

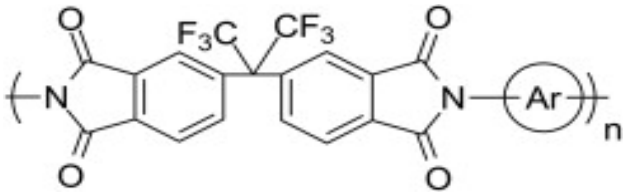


Figure 13 General structure of 6FDA-based aromatic polyimides (Ar represents the aromatic moieties in the diamide). [6]

1.3.3 Perfluoropolymers

Perfluoropolymers unlike other polymers have a great thermal and chemical resistivity and that allow them to be utilize in various applications. Moreover, they possess very high resistivity to plasticization which makes them candidates in natural gas purification. The bonds between carbon and fluorine atoms are very strong and this is the reason behind their unique properties. Although, the CO_2/CH_4 separation is not promising, there is a potential use in nitrogen rejection from natural gas as shown in Fig. 14 [17]. The perfluoro-polymers like Teflon, Hyflon and Cytopare commercialized by Membrane Technology and Research Inc. (MTR) under Z-top branch name. The gas transport properties of common fluorinated polymers are shown in Table 5 and the improvement of the performance is clear after fluorination.

Table 5 Chemical structure and glass transition temperature for some perfluoropolymers. [17]

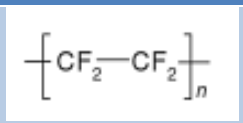
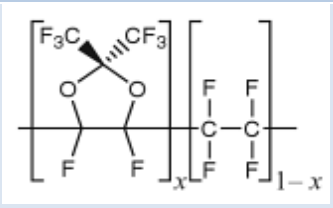
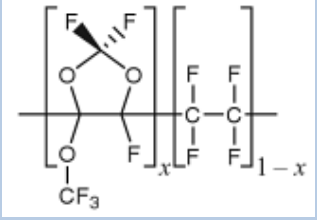
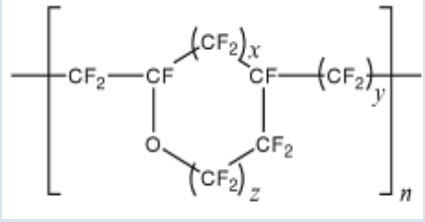
Polymer	Chemical Structure	Glass Transition Temperature (°C)
PTFE		30
Teflon AF		240
Teflon AD		134
Cytop		108

Table 6 Pure gas Permeabilities of some perfluoropolymers. [17]

Permeability (Barrer)	Teflon AF2400	Teflon AF1600	Hyflon AD80	Hyflon AD60	Cytop
He	--	--	430	390	170
H_2	2090	550	210	180	59
CO_2	2200	520	150	130	35
N_2	480	110	24	20	5
CH_4	390	80	12	10	2

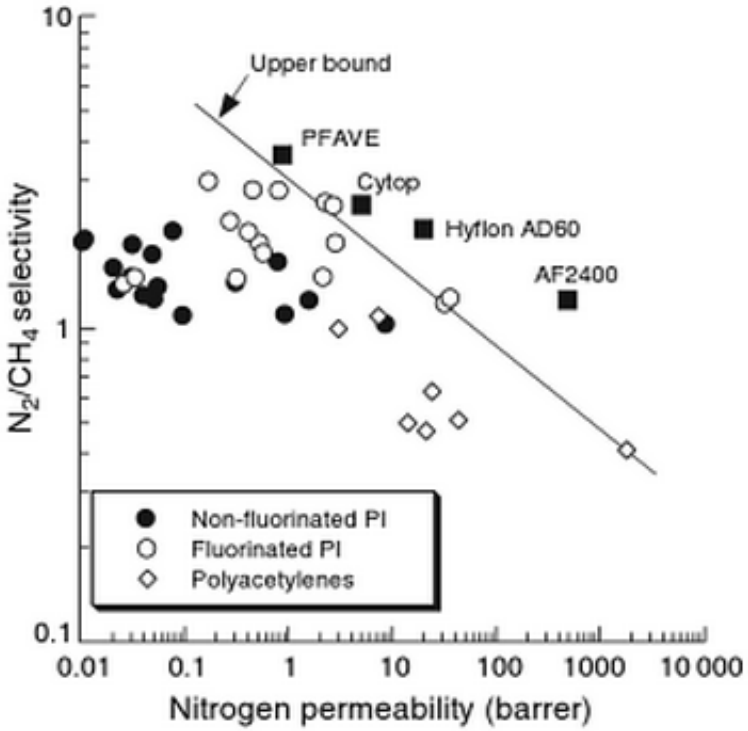
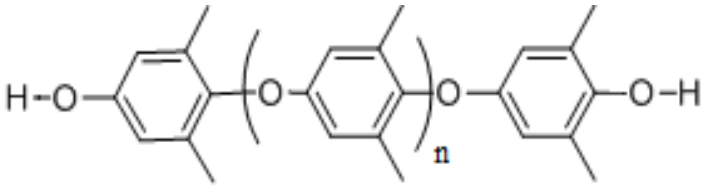


Figure 14 Nitrogen/methane selectivity-permeability trade-off relationships for some glassy polymer. [17]

1.3.4 Poly Phenylene Oxide

Poly Phenylene Oxide (PPO) possesses high permeability comparing to other glassy polymers. In addition, it has good mechanical properties. By looking to its structure, PPO has a linear structure consists of benzene ring attached to oxygen and to methyl groups. The rotational motion of the phenyl ring around the ether linkage has very low transition temperature. This is a preferred property from mechanical point view as the polymer will still have considerable ductility and impact resistance at low temperature. The fact that two methyl groups are attached to the aromatic ring, and the absence of any polar groups, has countered the chain packing and densification of the polymer matrix. This is advantageous for faster diffusion of gases. On the other hand, the methyl groups attached on both sides of the aromatic ring will prevent the free rotation of the phenyl ring leading to the moderate selectivity toward gases. PPO ideal selectivity for CO_2/CH_4 is around 16; its permeability is dependent on its molecular weight (40-90 Barrer). In mixture gas systems, selectivity observe is in the range 8-10. This is mainly due to competitive adsorption. PPO is found to be least interactive with CO_2 and for that it has high

resistivity to plasticization when compared to CA, Matrimid. One way to improve PPO performance is by chemical modification. For instant, some researches focus on attaching a bulky group like Bromine to the backbone which will stiffen it and increase the permeability. As shown in Table 7, the permeability almost doubled at degree of bromination of 60% without affecting the separation factor [18]. Moreover, different degree of bromination will result in different membrane performance. Other studies have dealt with different type of modification such as sulfonation. The sulfonic group is a polar group with a dipole moment as a result of the electro-negativity difference between the hydrogen atom and oxygen atom in the sulfonic group. This electro-negativity will lead to better packing density which results in lowering the free volume. As a result, the permeability will decrease sharply but the selectivity will increase due to the interaction of the gases with the dipole moment as shown in Table 8 [19].



poly(2,6-dimethyl-I,4-phenylene oxide)

Figure 15: Chemical structure of PPO. [6]

Table 7 Performance of brominated PPO membranes. [18]

	Gas permeability (Barrer)			Selectivity
	CO_2	CH_4	N_2	CO_2/CH_4
PPO	90	5.4	3.7	16.7
BPPO 60%	159.9	9.1	8	17.6

Table 8 Single gas permeability and selectivity of PPO membrane and its modified forms (feed pressure = 30 kg/cm^2). [19]

	Permeability (Barrer)		Selectivity
	CO_2	CH_4	(CO_2/CH_4)
PPO	43.7	3.6	12.1
SPPO	18.4	0.67	27.2

1.4 Promising Membrane Materials

1.4.1 Thermally Rearranged Polymers

Thermally rearranged polymer is a new family discovered by Dr. Lee and his team in Korea. TR polymers are aromatic polymers prepared by thermal conversion reaction of polyimide which has the functional group at ortho-position (figure 16). This reaction led to unique microstructure with specific cavity size which can be controlled by heat treatment [20]. TR polymer membranes are promising candidate for nature gas application especially for CO_2 separation due to its outstanding resistivity to plasticization. TR-1 polymer (which is derived from 6FDA+bisAPAF) is an example of the remarkable performance of TR polymer as it has both outstanding CO_2 permeability and CO_2/CH_4 selectivity [21]. Many other TR polymers showed a performance above the 2008 upper bound. As reported in [21] TR polymer from 1 to 6 were derived from the following polymer 6FDA+bisAPAF, OPDA + bisAPAF, BTDA + bisAPAF, BPDA + bisAPAF, PMDA+ bisAPAF and NTDA + bisAPAF respectively. Fig. 17 shows their promising performance for each on them comparing to the upper bound.

Thermally rearranged membranes are very difficult to process, expensive and hard to make hollow fiber out of it. Also, TR performance in mixed gas condition is low comparing to the pure gas cases. One of the most important factors that will affect the gas permeability dramatically is the heat treatment temperature. Fig. 18 shows the significant increase in permeability and the decrease in the separation factor with respect to final treatment temperature [21]. The procedure followed to prepare such membrane is first to heat the clean polyimide membranes up to around 300 ^{o}C to remove the solvent. After one hour, the temperature increased again to 450 ^{o}C for another hour to induce thermal rearrangement. Table 9 presents the effect of conversion percentage on the gas permeation properties.

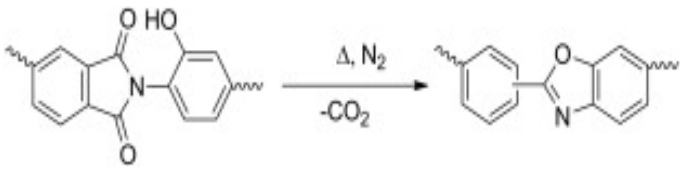


Figure 16 General scheme of thermal rearrangement (TR) of poly(hydroxyimide)s. [6]

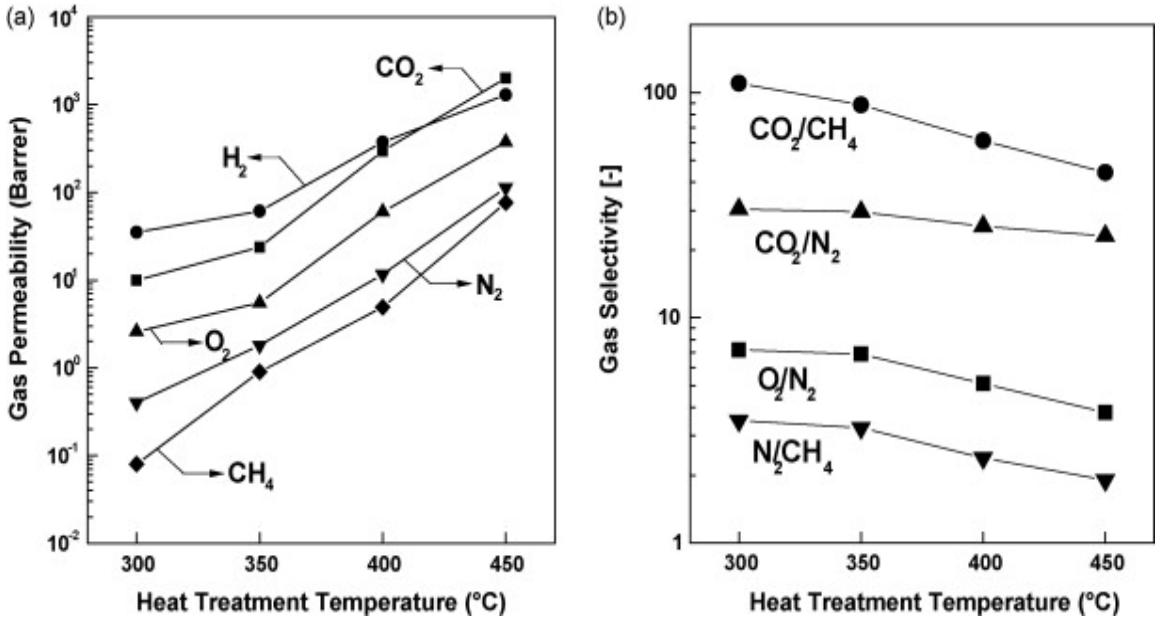


Figure 17 Gas permeability and (b) gas selectivity of TR-1 polymer membrane as a function of the heat treatment temperature. [21]

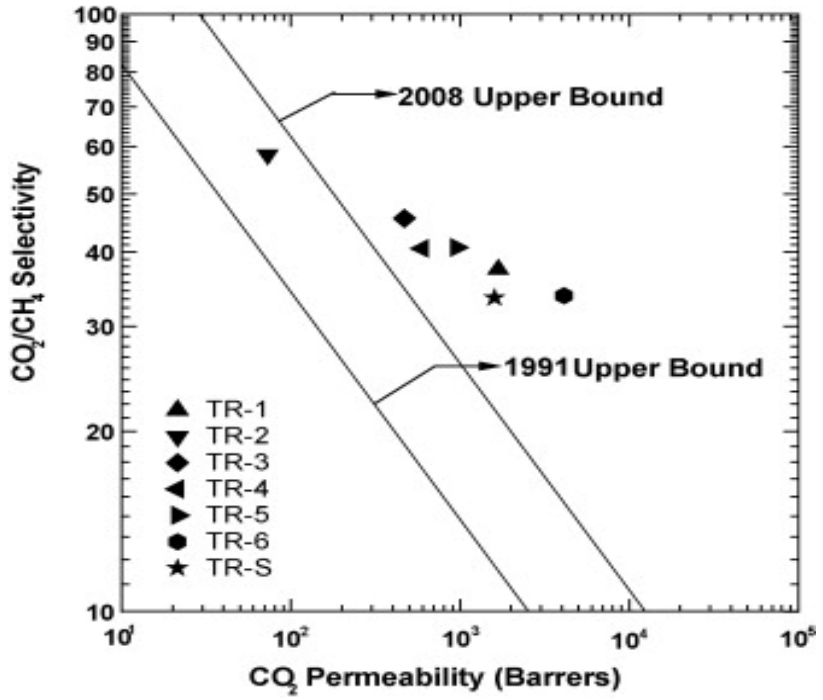


Figure 18 Relationship between CO_2 permeability and CO_2/CH_4 selectivity of TR polymer membranes. [21]

Table 9 Pure gas permeability (Barrer) of HAB-6FDA polyimide and TR polymers at 10 atm and 35 ^{o}C. [22]

Sample	Conversion (%)	CH_4	N_2	CO_2	H_2
HAB-6FDA	0	0.313	0.56	12.0	37.8
TR350	39	0.77	1.62	35.3	95
TR400	60	5.6	8.7	160	290
TR450	76	18.2	25.3	410	530

1.4.2 Polymer of Intrinsic Microporosity (PIMs)

Polymers of intrinsic micro-porosity have very rigid molecular structure which results in inefficient packing of the macromolecules. Therefore, the backbone movements will be restricted which gives unique properties for the polymer. Unlike TR polymer, the micro-porosity (pore diameter < 20 Å) is not derived through thermal treatment; it is derived from the molecular structure itself.

Among many PIMs, two of them were only commercially available which are PIM-1 & PIM-7 and their synthetic paths are shown in Fig. 19. Those two materials showed excellent performance for the separation of carbon dioxide from methane which places them above 2008 upper bound. But, like many other membrane material, its performance will drop in case of mixed gas conditions and figure 21 shows that clearly. However, there are several ways to modified PIMs and one common way is post-polymerization. This method involves introducing CO_2-philic functionalities on the main chain and that result in better interaction with CO_2. For instance, amidoxime–PIM-1 is synthesis by a reaction of nitrile group with hydroxyl amine as shown in Fig. 20 [23]. This modification improves the CO_2/CH_4 selectivity by factor of two but that affect the productivity of the membrane as shown in Table 10 and figure 21 [31].

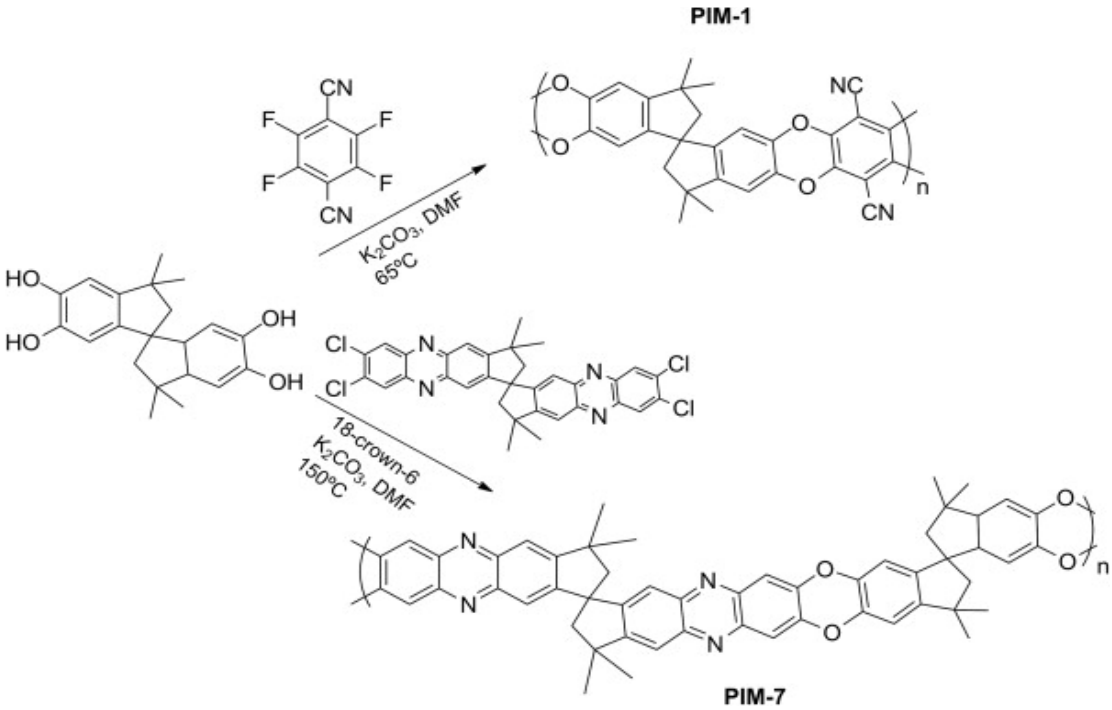


Figure 19 Synthesis and chemical structures of PIM-1 and PIM-7. [31]

Table 10 Comparison between PIM-1 & AO-PIM-1(T=35 °C, 2 bar; 24 h methanol soak; dried under vacuum at 120 °C for 24 h). [23]

Polymer	Permeability (Barrer)			Selectivity
	N_2	CH_4	CO_2	CO_2/CH_4
PIM-1	248	362	5919	14
AO-PIM-1	33	34	1153	34

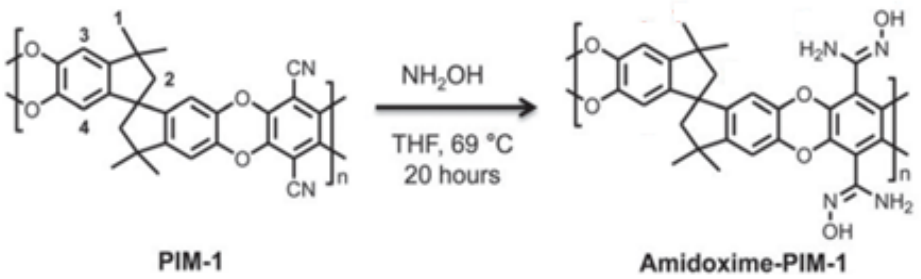


Figure 20 Molecular structures and synthetic pathway of AO-PIM. [23]

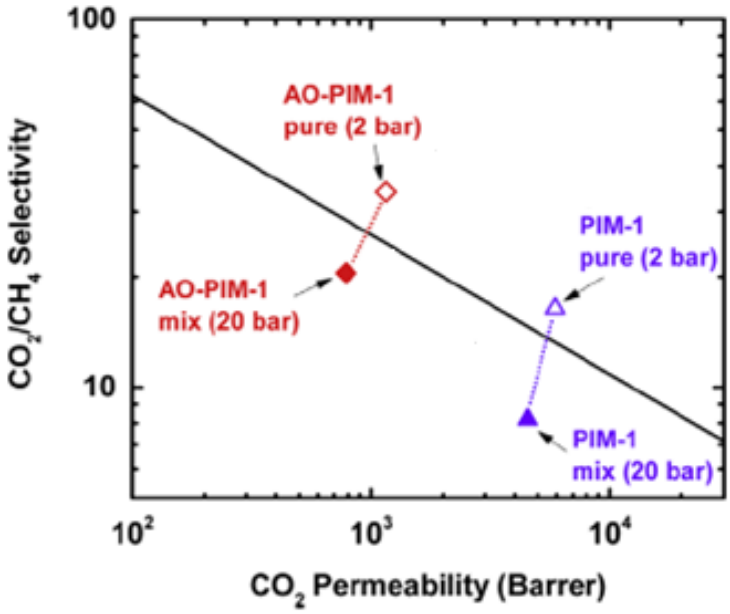


Figure 21 Comparison between PIM-1&AO-PIM-1 performances under pure and mixed gas condition. [23]

1.4.3 Mixed Matrix Membranes

One way to enhance the membrane performance is to add an inorganic material to the polymer matrix and that is known as mixed matrix membrane. These inorganic materials should have unique properties in order for it to improve the resultant membrane. The fabrication of this type of membranes is not straight forward because it is difficult to make strong connection between the inorganic particles and the polymer itself [16]. Several parameters need to be control to get good membranes, for instance, particle size and particle pore size must be optimized. In addition, the particles distribution within the polymer matrix is very critical to get defect-free membrane. The procedure followed to make a MMM is the same as other regular membrane except that before casting, polymer/filler/solvent mixture should be prepared first. Zeolite, fumed silica and activated carbon are some example of inorganic particles used as dispersed phase in MMM for gas separation. Depending on the type of the filler and its weight percentage, both permeability and selectivity can be improved significantly. For instant, Ref. [24] used activated carbon as filler in an acrylonitrile-butadiene-styene membrane. As a result, CO_2 permeability and CO_2/CH_4 separation factor increase by double in the resultant MMM. More examples are shown in Table 11 for different materials. One limitation of using MMMs in natural gas separation is because it contains some moisture that can block the pores. In addition, MMMs are difficult to be processed into hollow fiber module with thin thickness.

Table 11 Comparison between some MMMs and their neat polymers. [24]

Polymer	Filler	Neat Polymer		MMMs	
		CO_2 Permeability	α CO_2/CH_4	CO_2 Permeability	α CO_2/CH_4
Matrimid	**CMS** (36 vol%)	10 Barrer	35.3	12.6 Barrer	51.7
ABS	**AC** (62.4 vol%)	2.5 Barrer	24	6.67 Barrer	50
PES	**Zeolite+silver** ion exchange (50wt%)	1 Barrer	35.3	1.2 Barrer	44

1.4.4 Carbon Molecular Sieve

Carbon membrane has a great potential for gas separation application. They possess an outstanding ideal selectivity probably more than any known membrane. In addition to that, their mechanical strength is excellent so they can handle high pressure difference. Moreover, they are thermally very stable even at high temperature, up to 900 ^{o}C. On the other hand, carbon molecular sieve membranes are very brittle and fragile. Therefore, it is difficult to process and expensive to fabricate. The fabrication of carbon membranes depends on several factors such as precursor selection, polymeric membrane preparation, pre-treatment, pyrolysis, and post treatment. Suitable precursor materials will not cause any pore-holes or cracks to appear after the pyrolysis step. Precursor membranes must be prepared in defect free form in order to minimize problems during the manufacture of carbon membranes. Pyrolysis is a process in which a suitable carbon precursor is heated in a controlled atmosphere in a furnace (Fig. 22) to the pyrolysis temperature at a specific heating rate for a sufficiently long thermal soak time. In order to meet the desired pore structure and separation properties of carbon membranes, post treatment methods have been applied.

Nitrogen is the hardest gas to remove from natural gas. The reason for that is because N_2 and CH_4 have almost the same properties. On one hand, methane is larger than nitrogen, on the other hand, methane is more condensable than N_2. As a result, the separation factor between the two is low (usually less than 3). CMS membranes show a very attractive separation with N_2/CH_4 selectivity more than 7. In [27] Matrimid was pyrolyzed at different temperature to produce carbon molecular sieve membrane. An increase by factor of seven in the separation factor at pyrolysis temperature of 800 ^oC was observed. However, the relation between the final temperature and the permeability or selectivity is not straight line. Figure 23 shows how the Matrimid performance can vary depending on the pyrolysis temperature.

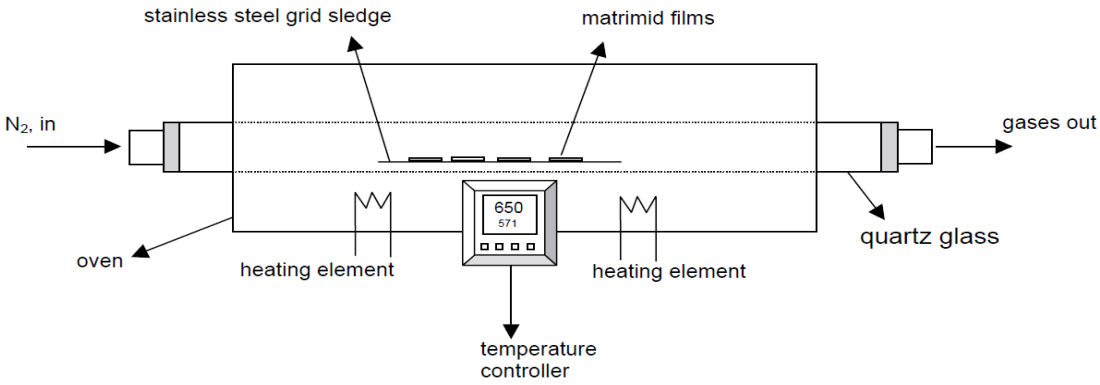


Figure 22 Schematic of the furnace used. [6]

Table 12 Matrimid performance at initial condition and at 800 ^oC pyrolysis. [27]

Precursor	Pyrolysis Temperature	Thermal soak	Feed pressure	Feed temperature	P N_2	P CH_4	α N_2/CH_4
Matrimid 5218	no pyrolysis	NA	65 psi	35°C	0.32	0.28	1.14
	800 °C	2 h		25°C	5.62	0.68	8.27
				35°C	6.78	0.88	7.69
				50°C	8.98	1.19	7.57

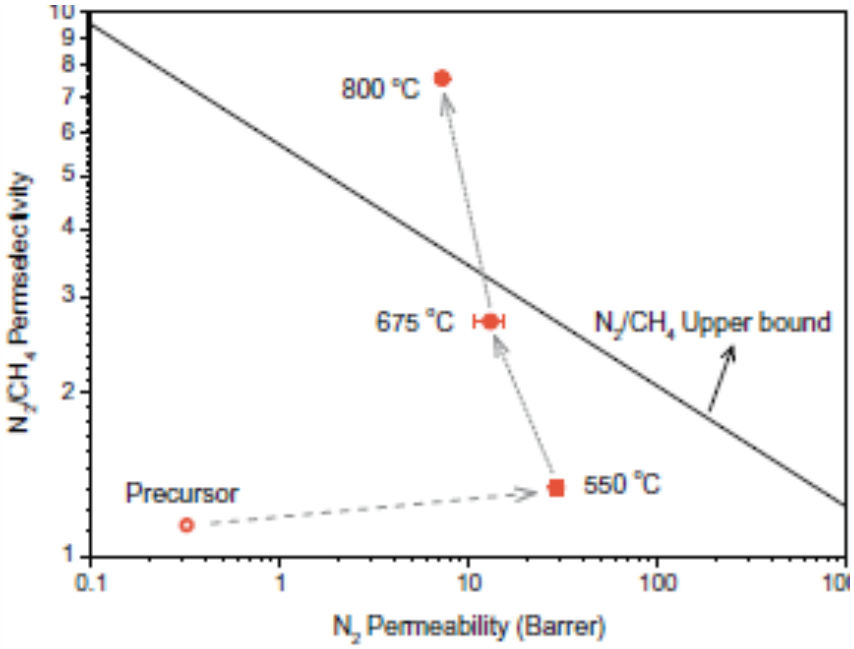


Figure 23 Matrimid 5218 was pyrolyzed under inert argon to produce carbon molecular sieve (CMS) dense film membranes. [27]

1.5 Thesis Objective

The main objective is to develop a high-performance membrane (both high permeability and selectivity) for natural gas separation application. Based on comprehensive literature review covering all types of gas separation membranes like mixed matrix membranes, Carbon membranes, perfluoropolymers, polyimide and many other families, the decision was made to study thermally rearranged polymer due to its outstanding performance as shown in figure 24. However, there are a lot of parameters that need to be studied when it comes to this type of polymer and it is almost missing in the existing literature. Therefore, the objective is to study and develop thermally rearranged membrane and focus on covering whatever is missing in previous art including:

1. Mixed gas data, including the following parameters:
    a) Effect of pressure
    b) Effect of pressure ratio.
    c) Effect of stage cut.

2. Testing under high pressure (up to 800 psi).
3. Plasticization resistivity.

By achieving this objective can help in taking thermally rearranged polymer one big important step forward toward the industrial application deployment for natural gas separation purposes. Moreover, if this technology gets commercialized it will have a big impact on the gas processing industry as a whole because it will debottleneck the existing Amine absorption units. More importantly, it will provide an economical feasible solution to start producing gas from undeveloped gas wells due to high acid gas content which are called unconventional gas resources.

CHAPTER 2

LITERATURE REVIEW: THERMALLY REARRANGED POLYMERS

Thermally rearranged polymers are aromatic polymers prepared by thermal conversion reaction of polyimide or polyamide which has the functional group at ortho-position. This reaction converts the precursor polymer into rigid structure, which leads to unique microstructure with specific cavity size. Heat treatment of the polymer can further control the cavity size [21, 30]. After the gas molecules get adsorbed in the polymer matrix; they have to diffuse throughout the thickness of the membrane. Due to the difference between the gas molecules sizes and the membrane cavities, the separation will occur where small gas molecules will pass through those cavities and the large ones are rejected. TR polymers exhibit interesting cavity size distribution that provides high selectivity between gases like CO_2 and CH_4. Additionally, they have relatively high free volumes which provide desirable high flux. This combination of both high selectivity and permeability along with rigid structure which resist plasticization make them an excellent candidate for natural gas purification. One advantage of TR polymers is the flexibility of designing different cavity sizes by controlling the treatment temperature and the polymer structure [31]. Figure 24 shows one example of the outstanding performance of multiple TR polymers for CO_2/CH_4 separation [21]. However, TR polymer is sensitive to any moisture or liquid in the feed, so proper pretreatment is needed.

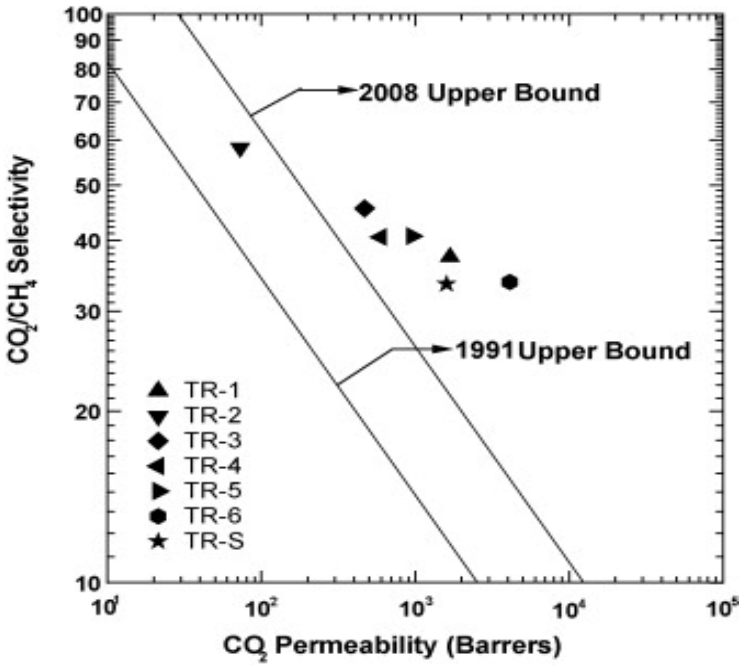


Figure 24 Relationship between CO_2 permeability and CO_2/CH_4 selectivity of TR polymer membranes. [21]

2.1 The Structure Rearrangement Mechanism

There are several studies that tried to understand the exact mechanism for the thermal reaction that occur during the TR synthesis; however, it is not fully understood. Many researchers believe that the hydroxyl group in the polyimide will thermally rearrange to polybenzoxazol. Figure 25 shows the expected mechanism of this thermal rearrangement. As a starting point, polyimide should contain a hydroxyl group [33]. Then, hydroxyl-imide ring rearranged to a carboxyl-benzoxazole intermediate followed by decarboxylation. The final product will be a fully aromatic benzoxazole at a temperature between 350 and 450 ^{o}C.

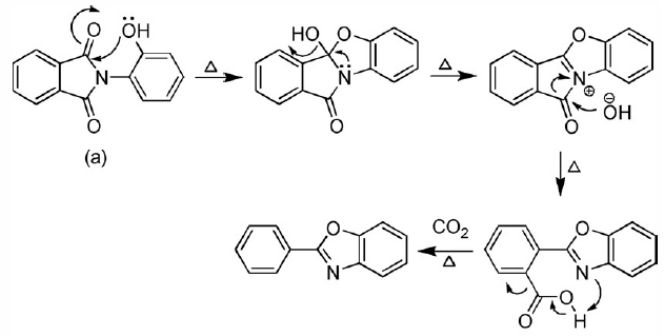


Figure 25 The mechanism of thermal rearrangement of hydroxyl-containing polyimide to polybenzoxazole. [33]

This rearrangement will result in formation of nano-porous cavities. The size of those cavities is controlled by the rearrangement temperature. Furthermore, the free volume of the TR polymer is much higher than the original polyimide and that explains the increase in the permeability of different gas components. However, a group of researchers in Australia don't believe that hydroxyl-containing polyimides to polybenzoxazoles thermal reaction take place. The FTIR analysis that they have are not compatible with the proposed reaction mechanism. The new work designate that H_2O were lost from the hydroxyl group rings which will result in benzene units. Then, the benzene units will dimerize to abiphenylene units as shown in Figure 26.

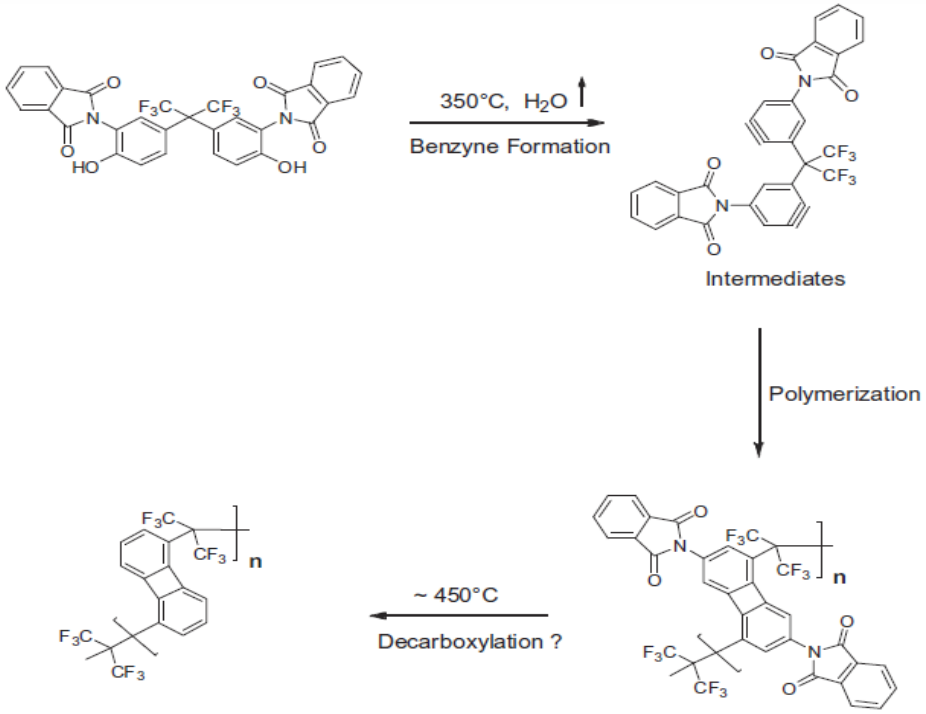


Figure 26: New proposed reaction mechanism for thermally rearranged polymer. [34]

This argument can be addressed and understand in the following points:

1. The best way to exactly indicate the chemical structure of any material is by NMR. However, it is almost not possible to run NMR test in thermally rearranged polymer obtained from polyimide because it is not soluble in any solvent. So, NMR test can be used as a characterization method.
2. Using FTIR spectra will not show strong evidence of occurrence of either mechanism. The reason for that is because the absorbance levels are weak. So, FTIR alone can't be the only way to judge.
3. Huan Wang successfully produced the same thermally rearranged polymer from two different based materials one is polyimide and the other is polyamide as shown in Fig. 27 [35]. Since, TR polymer prepared from polyamide is soluble in chloroform, NMR test was done and the result indicated the existence of polybenzoxazol structure. The thermal reaction of polyamide involved the loss of H_2O.
4. By looking to the TGA result of the two TR polymers prepared by Huan Wang, it is clear that the mass losses at two different temperatures. Since, the rearrangement of polyamide required the loss of H_2O, it can be concluded the rearrangement of polyimide involve CO_2 release which is the first mechanism.

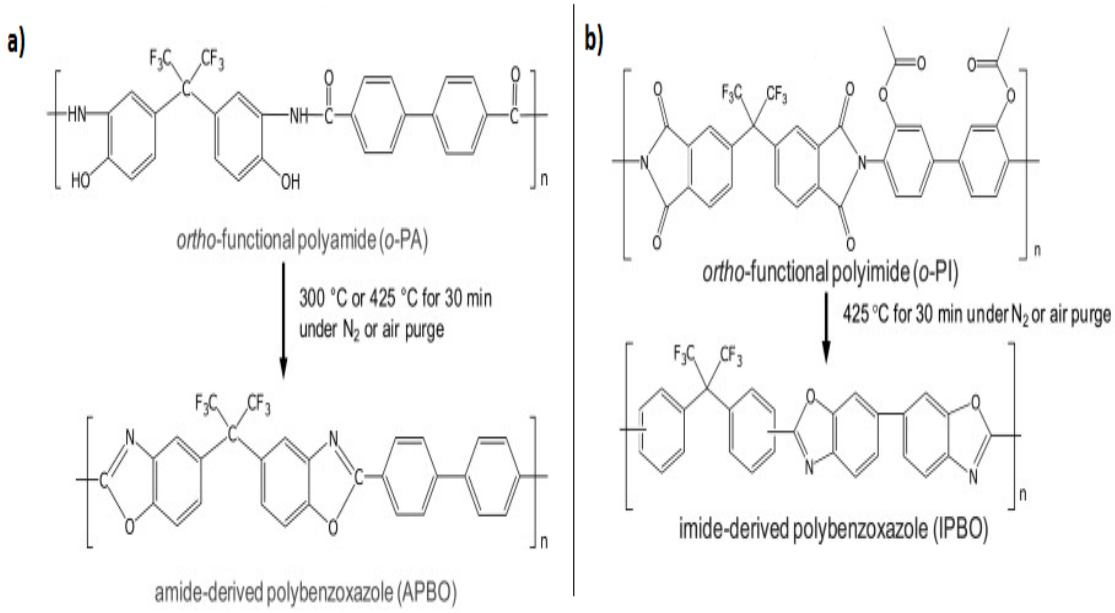


Figure 27 The same TR polymer obtained from a) polyamide and b) polyimide. [35]

2.2 TR Polymers Derived from Polyimide

Thermally rearranged polymers can be produced from either polyimide or polyamide with a certain functional group. If the precursor of TR polymer is polyimide, it is called TR-α polymer which has heterocyclic rings. Depending on the functional group at the ortho position, different type of TR polymer can be achieved like polybenzoxazoles (PBO), polypyrrolone (PPL), polybenzothiazoles (PBZ) and polybenzimidazoles (PBI) as shown in Fig 28. The precursorsare synthesized by conventional polycondensation reaction of dianhydride and diamine with functional group at ortho position. Furthermore, there are different imidization methods such as thermal, chemical and azeotropic and that will have an impact on the resultant TR polymer and its physical properties but not the thermal conversion pathway [36, 37].

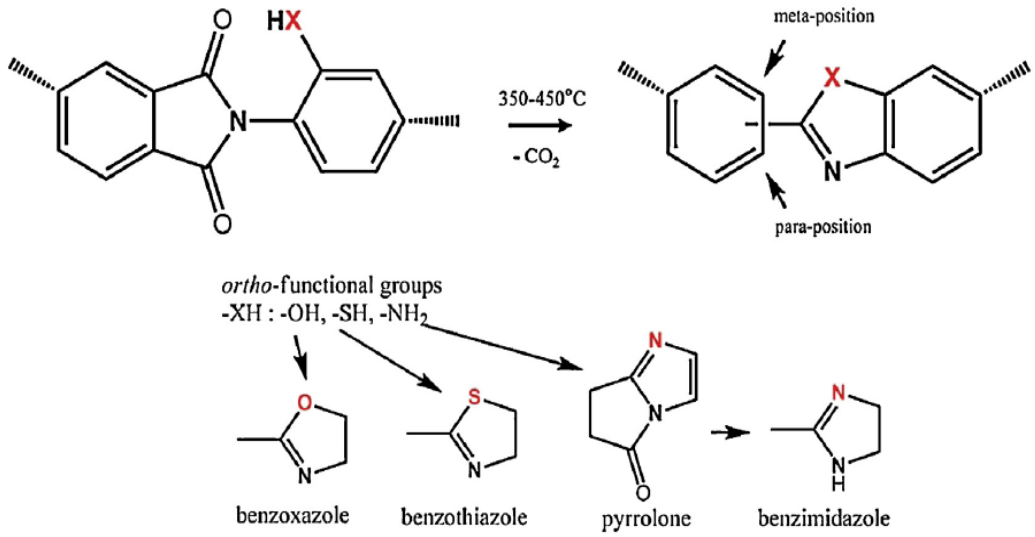


Figure 28 Thermal rearrangement mechanism of TR-α polymer. [31]

There are many studies that focused on TR polymer especially TR-PBO obtained from hydroxyl polyimide (HPI). In addition to the chemical structure and synthesis routs, the degree of thermal rearrangement depends on the temperature and the reaction time. Moreover, the degree of conversion is not in a linear relationship with treatment temperature. All of these factors have a direct impact on the gas transportation properties of TR polymer membranes. Table 13 shows gas permeability and selectivity of most studied TR-α polymer membranes [31].

Table 13 Gas permeability and selectivity of TR-α polymers.

Polymer Code	Structure	Permeability (Barrer)					Selectivity				Ref.
		H_2	CO_2	O_2	N_2	CH_4	CO_2/CH_4	CO_2/N_2	N_2/CH_4	O_2/N_2	
TR-α-PBO											
TR-1	**6FDA+ bisAPAF**	2774	4045	747	156	73	55.41	25.93	2.14	4.79	***21***
TR-2	**BPDA+ bisAPAF**	444	597	93	20	15	39.80	29.85	1.33	4.65	
TR-3	**ODAP+ bisAPAF**	91	73	14	2.3	1	73.00	31.74	2.30	6.09	
TR-4	**BTDA+ bisAPAF**	356	469	81	15	10	46.90	31.27	1.50	5.40	
TR-5	**PMDA+ bisAPAF**	635	952	148	34	23	41.39	28.00	1.48	4.35	
TPBO	**6FDA+ bisAPAF**	4194	4201	1092	284	151	27.82	14.79	1.88	3.85	***37***
APBO	**6FDA+ bisAPAF**	408	398	81	19	12	33.17	20.95	1.58	4.26	
CPBO	**6FDA+ bisAPAF**	3612	5568	1306	431	252	22.10	12.92	1.71	3.03	
CPBO	**6FDA+ bisAPAF**	3585	5903	1354	350	260	22.70	16.87	1.35	3.87	
TR400	**6FDA+ HAB-EA**		51			1.4	36.43				***38***
TR400	**6FDA+HAB-Ac**		174			5.1	34.12				
TR400	**6FDA+HAB-Pac**		211			11.4	18.51				
TR450	**6FDA+HAB**	530	410	100	25.3	18.2	22.53	16.21	1.39	3.95	***39***
APAF-6FDA	**6FDA+APAF**	1665	1993	474	154	115	17.33	12.94	1.34	3.08	***40***
APAF-BTDA	**BTDA+APAF**	229	149	31	6.5	3.9	38.21	22.92	1.67	4.77	
APAF-ODPA	**ODAP+APAF**	188	112	26	5.3	3.2	35.00	21.13	1.66	4.91	

PBO	**6FDA+HAB**	407	296	62.7	14.3	9.2	32.17	20.70	1.55	4.38	
	6FDA+HAB(95)+ bisAHPF(5)	1189	1079	227	57.1	41.7	25.88	18.90	1.37	3.98	
	6FDA+HAB(90)+ bisAHPF(10)	1479	1539	316	83.6	65	23.68	18.41	1.29	3.78	***41***
CPBOC	**6FDA+HAB(85)+ bisAHPF(15)**	1254	1306	264	69.3	58.7	22.25	18.85	1.18	3.81	
CPBO	**6FDA+ bisAHPF(cardo)**	371	255	54.2	11.8	9.2	27.72	21.61	1.28	4.59	
PHAB-6FDA	**6FDA+HAB PI**	35	10	2.3	0.35	0.16	62.50	28.57	2.19	6.57	
PTR450	**6FDA+HAB PBO**	260	240	45	10	7.7	31.17	24.00	1.30	4.50	***42***
MHAB-6FDA	**6FDA+mHAB PI**	46	12	2.8	0.41	0.18	66.67	29.27	2.28	6.83	
MTR450	**6FDA+mHAB PBO**	570	720	130	34	31	23.23	21.18	1.10	3.82	
TR-PBO	**6FDA+bisAPAF**	294	261	52.5	12.6	7.5	34.80	20.71	1.68	4.17	
XTR-PBO-5	**6FDA+bisAPAF+ DABA(5)**	603	746	133	29.6	19.9	37.49	25.20	1.49	4.49	
XTR-PBO-10	**6FDA+bisAPAF+ DABA(10)**	763	980	193	50.9	33	29.70	19.25	1.54	3.79	***43***
XTR-PBO-15	**6FDA+bisAPAF+ DABA(15)**	515	668	119	29.8	19.4	34.43	22.42	1.54	3.99	
XTR-PBO-20	**6FDA+bisAPAF+ DABA(20)**	421	440	81.9	19.7	12.4	35.48	22.34	1.59	4.16	
TR-α-PEBO											
450-1	**6FDA + 6FBAHPP**	95.3	41.4	10.0	1.89	1.45	5.3	22	29	2.3	***44***
450-3	**6FDA + 6FBAHPP**	439	486	88.5	20	17	4.4	24	29	0.9	
TR-α-PBI											
PBI	**6FDA + DAB**	1779	1624	337	62.0	35	5.4	26	46	1.1	***45***

2.3 TR Polymers Derived from Polyamide

Thermally rearranged polymers can also be obtained from polyamide precursors which are produced through polycondensation reaction of diacid chloride and hydroxyl diamines. The thermal reaction of TR polymer produced from polyamide, called TR-β, is usually carried out at a temperature lower than TR-α. The thermal rearrangement mechanism of TR-β is shown in Fig. 29.

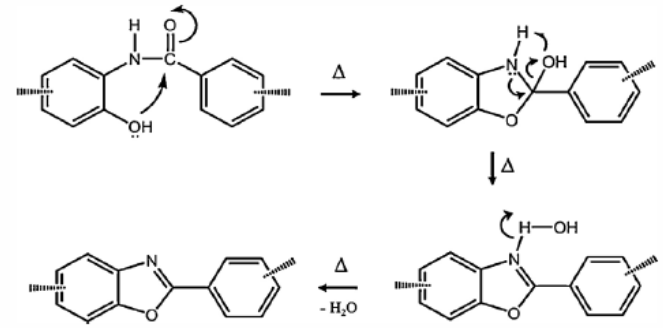


Figure 29 Thermal rearrangement mechanism from hydroxyl polyamide to polybenzoxazole. [31]

TR-β polymers exhibit attractive gas separation properties for the small gases like H_2 and CO_2. Just like the TR derived from polyimides, the membrane performance of TR-β is directly impacted by the degree of thermal cyclization which is related to the treatment temperature as shown in Fig. 30 [46]. Nevertheless, there are a limited number of studies that have dealt with TR polymer produced from polyamide and table 14 summarizes those attempts.

Table 14 Gas permeability and selectivity of TR-α polymers

Polymer Code	Structure	Permeability (Barrer)					Selectivity				Ref.
		H_2	CO_2	O_2	N_2	CH_4	CO_2/CH_4	CO_2/N_2	N_2/CH_4	O_2/N_2	
TR-β											
MPBO	IPCl + bisAPAF	65	22	6.4	0.4	0.5	44.00	55.00	0.80	16.0	
PPBO	TPCl + bisAPAF	128	72	17	3.2	1.9	37.89	22.50	1.68	5.31	*47*
6FPOB	6FCl + bisAPAF	65	44	11	5.6	1.5	29.33	7.86	3.73	1.96	
PBO450	BPDC + bisAPAF	526	532	105	30.3	28.9	18.41	17.56	1.05	3.47	*35*

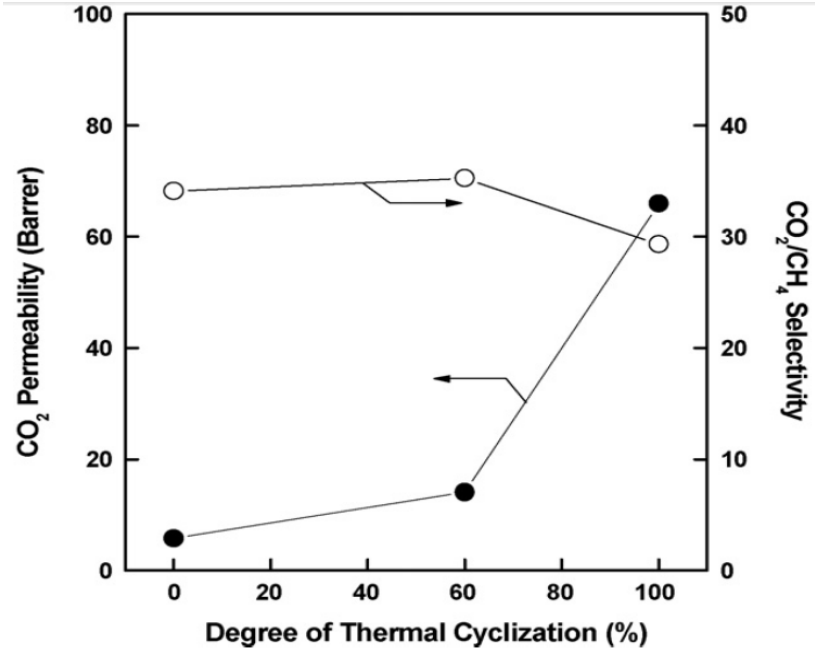


Figure 30 CO_2 permeability and CO_2/CH_4 selectivity of fluorinated polybenzoxazole membrane as a function of degree of thermal cyclization. [46]

2.4 TR Co-Polymers

Just like various polyimide and polyamide, many thermally rearranged copolymers have been investigated for gas separation applications. TR poly(benzoxazole-co-pyrrolone) (TR-PBO-co-PPL) showed an increase in CO_2/CH_4 selectivity, more than double in some cases, comparing to the original individual TR-PBO and TR-PPL. Furthermore, TR-α, β copolymers have been studied to improve the gas separation properties which was not the case; however, the processability of the membrane improved. Table 15 shows the TR copolymers that have been investigated so far.

Table 15 Gas permeability and selectivity of TR copolymers.

Polymer code	Structure	Permeability (Barrer)					Selectivity				REF
		H_2	CO_2	O_2	N_2	CH_4	CO_2/CH_4	CO_2/N_2	N_2/CH_4	O_2/N_2	
TR-α-PBO-co-PI											
TR-PBO	BPAD + bisAPAF	1228	1014	220	48	41	24.7	21.1	1.17	4.58	
TR-PBO-co-PI	BPAD + bisAPAF(8) + ODA(2)	623	389	90	18	14	27.8	21.6	1.29	5.00	
	BPAD + bisAPAF(5) + ODA(5)	47	25	4.8	0.82	0.65	38.5	30.4	1.26	5.85	***34***
	BPAD + bisAPAF(2) + ODA(8)	38	11	2.2	0.4	0.3	36.7	27.5	1.33	5.50	
PI	BPDA + ODA	14	2.7	0.72	0.09	0.03	90.0	30.0	3.00	8.00	
PBO-MDA	ODPA + bisAPAF(8) + MDA(2)	43.4	18	3.9	0.66	0.41	43.9	27.2	1.61	5.91	
PBO-DAM	ODPA + bisAPAF(8) + DAM(2)	53.2	23.5	4.99	0.79	0.43	54.6	29.7	1.84	6.32	
PBO-OT	ODPA + bisAPAF(8) + OT(2)	47.3	16.8	3.45	0.57	0.32	52.5	29.5	1.78	6.05	***48***
PBO-BAP	ODPA + bisAPAF(8) + BAP(2)	31.2	11.9	2.39	0.39	0.22	54.1	30.5	1.77	6.13	
PBO-BAPP	ODPA + bisAPAF(8) + BAPP(2)	40.4	18.8	3.48	0.62	0.41	45.8	30.3	1.51	5.61	
PBO	ODPA + bisAPAF	44.9	15.7	3.95	1.25	1.74	9.02	12.6	0.72	3.16	
HAB:4MPD 3:1	6FDA + HAB(3) + 4MPD(1)		19		0.9	0.48	39.6	21.1	1.88	0.00	
HAB:4MPD 1:1	6FDA + HAB(1) + 4MPD(1)		52		2.3	1.2	43.3	22.6	1.92	0.00	***49***
HAB:4MPD 1:3	6FDA + HAB(1) + 4MPD(3)		226		11	5.8	38.9	20.5	1.90	0.00	

HAB:FDA 3:1	6FDA + HAB(3) + FDA(1)		14		0.94	0.59	23.7	14.9	1.59	0.00	
HAB:FDA 1:1	6FDA + HAB(1) + FDA(1)		23		1.4	1.04	22.1	16.4	1.35	0.00	
HAB:FDA 1:3	6FDA + HAB(1) + FDA(3)		36		2.6	1.47	24.5	13.8	1.77	0.00	
TR-α-PBO-co-PPL											
TR-PBO	6FDA + bisAPAF	4194	4201	1092	284	151	27.8	14.8	1.88	3.85	
TR-PPL	6FDA + DAB	376	234	65	13	8.1	28.9	18.0	1.60	5.00	
TR-PBO-co-PPL	6FDA + bisAPAF(8) + DAB(2)	1989	1874	421	94	50	37.5	19.9	1.88	4.48	***50***
	6FDA + bisAPAF(5) + DAB(5)	2895	1805	475	85	46	39.2	21.2	1.85	5.59	
	6FDA + bisAPAF(2) + DAB(8)	1680	525	132	18	6.7	78.4	29.2	2.69	7.33	
PHBOA(8:2)	IPCI + HAB(8) + ODA(2)	1.8	0.22	0.07	0.009	0.008	27.5	24.4	1.13	7.78	
PBOA(8:2)	IPCI + HAB(8) + ODA(2)	3.42	0.64	0.15	0.024	0.017	37.6	26.7	1.41	6.25	***51***
PHBOA(2:8)	IPCI + HAB(2) + ODA(8)	2.76	0.36	0.1	0.01	0.007	51.4	36.0	1.43	10.0	
PBOA(2:8)	IPCI + HAB(2) + ODA(8)	4.6	0.68	0.22	0.025	0.013	52.3	27.2	1.92	8.80	
TR-α,β-PBO											
PIBO300	TAC + bisAPAF	104	30.2	8.93	1.53	0.69	43.8	19.7	2.22	5.84	***52***
PBO400	TAC + bisAPAF	663	456	98.1	23.8	17.4	26.2	19.2	1.37	4.12	

CHAPTER 3

EXPERIMENTAL PROCEDURES

3.1 Material Selection

Based on a comprehensive literature review on all polymeric membrane types, thermally rearranged polymer has been chosen as the propose membrane material for my research due to its outstanding performance for natural gas separation. In addition to superior performance, there is a lack of studies on those types of membranes especially under mixed gas condition at relatively high pressure. The gas permeation result could vary significantly in those different conditions and that is why it crucial to study this effect.

The thermally rearranged polymers are polyimide polymers with unique chemical structure which gives a wide range of starting material to choose from. Based on a literature review specific to thermally rearranged membrane for gas separation, 6FDA-DAB polymer was chosen as my starting polymer for the following reason:

I. One of the best TR polymers for gas separation application.
II. There is a clear lack of research for this type polymer.
III. It is 6FDA-based polymer which usually has good thermal and mechanical properties.

3.2 Experimental

3.2.1 Materials

4 4'-(hexafluoroisopropylidene) diphthalic anhydride (6FDA, > 99%) purchased from Alfa Aesar, 3,3′-Diaminobenzidine (DAB, > 99%) and 1-methyl-2-pyrrolidinone (NMP) both purchased from Sigma-Aldrich.

3.2.2 Synthesis of 6FDA-DAB Precursor

The polypyrrolone was synthesized by the following procedure: 5 mmol of 3,3-diaminobenzidine was added to three-neck round-bottom flask followed by 10 ml of NMP and left under N_2 at 60 ^oC and stirrer for 2h until it completely dissolved. Meanwhile, 5 mmol of 4,4'-(hexafluoroisopropylidene) diphthalic anhydride was dissolved in 20 ml of NMP as well. After that, the 6FDA solution was slowly added to the three-neck round-bottom flask and the temperature was increased to 80 ^oC to impede an outbreak gelation by the drastic reaction of tetraamine with highly reactive dianhydride [9]. After stirring for 12 hours, the reaction was stopped and the resultant (poly(amino amicacid)) solution was filtered through 0.45 µm Nylon filters, then casted into membranes. The membranes were placed in vacuum oven at 80 ^oC for 24 h until they solidified, then the temperature was increased to 200 ^oC under vacuum to remove the residual solvent. The resulting dry poly(amino amic acid) (PAAc) membranes were placed in a furnace under vacuum at a temperature of 250 ^oC to thermally imidize the membranes to produce polyaminoimide (PAI) membranes as shown in figure 31 [45].

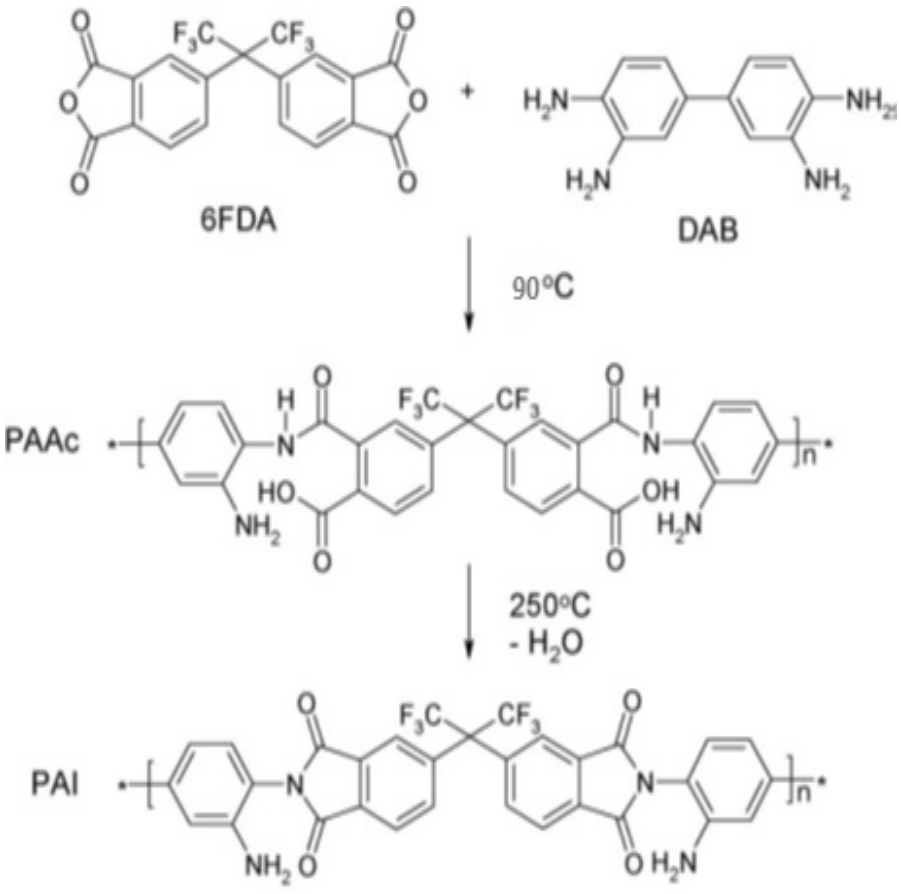


Figure 31 The proposed synthesis route to for 6FDA-DAB precursor. [45]

3.2.3 Thermal Reaction

The thermal treatment was done at different temperatures (300, 350, 400 and 450 ^{o}C) to produce PPL membranes as proposed in [45] and shown in figure 32, H_2O will be lost during this process. Depending on the final treatment temperature the degree of conversion can be controlled; in all cases the heating rate was kept at 2 ^{o}C/min with vacuum and the final temperature was held for one hour before the heating element was switched off. The thermal reaction was carried over in a tube furnace (Carbolite, UK) with a maximum temperature of 1200 ^{o}C.

In order to produce PBI membrane several more steps are required. The PPL (450) membrane was treated with 1 M NaOH solution at 100 ^{o}C for three hours (alkaline treatment). After that, the membrane was washed several times with water and then was kept in 0.1 M of HCl for 12 h. Subsequently, the resultant iPBI membrane was washed with water and dried under vacuum at 150 ^{o}C for 12 h. Finally, the iPBI membrane was treated again at 450 ^{o}C for 2 hours under vacuum to produce PBI membrane.

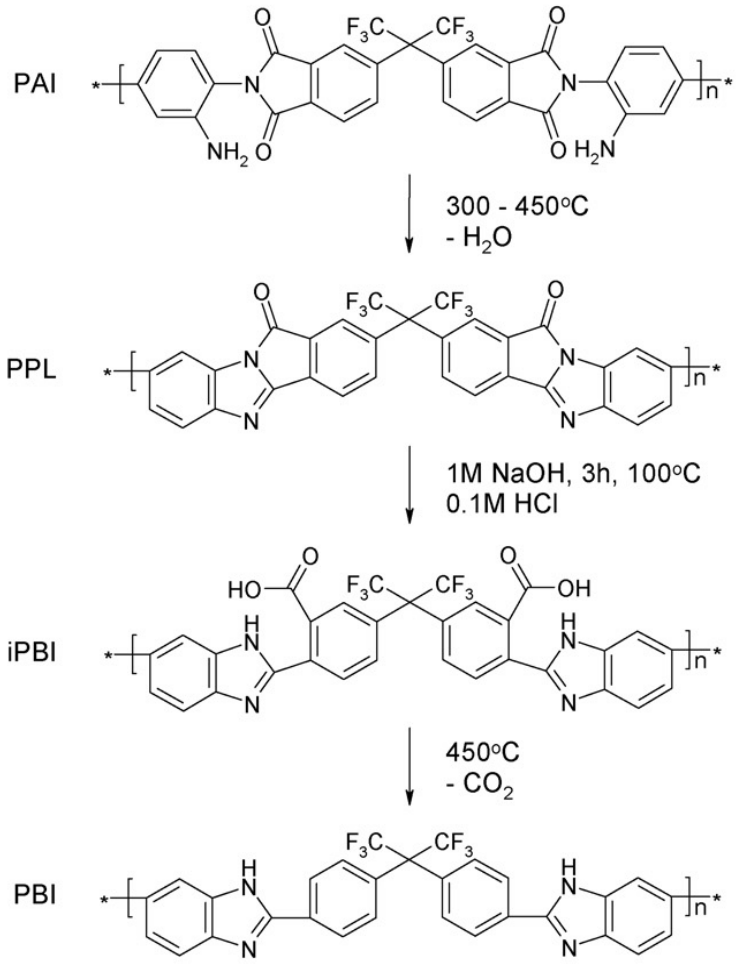


Figure 32 The proposed synthesis route to produce PPL & PBI by thermal treatment. [45]

3.3 Membrane Characterization

Membranes structures were investigated by Fourier Transform Infra-Red (FTIR) spectra (Thermo Scientific, USA) with a range of 4000-500 cm^{-1}. Thermal analysis such as thermogravimetric analysis (TGA) and DSC were performed by Simultaneous TG-DTA/DSC Apparatus (STA 449 F3 Jupiter, NETZSCH).

3.4 Pure Gas Permeation Measurement

Pure gas permeation data were measured by using a constant volume (high vacuum time lag) method. The setup is equipped by Omega pressure transducer with a range from 0 to 5 psia and 0.08% accuracy. In all experiments the order of the gases being tested was as follow: He, H_2, O_2, N_2, CH_4 and finally CO_2, so condensable gases are always at the end to prevent any effect on other gases result. The permeability measurement was done by introducing a gas to the upstream of membrane film at pressure of p_o. The downstream side has a known fixed volume and a pressure traducer to measure the pressure increase due to gas permeation through the membrane area A. the permeability for a test gas was calculated by the following formula:

$$P = \left(\frac{VT_oL}{p_oTA\Delta p}\right)\left[\left(\frac{dp}{dt}\right)_{ss} - \left(\frac{dp}{dt}\right)_{leak}\right] \quad (8)$$

where P is the permeability in Barrer (1 Barrer = 10^{-10} cm^3 (STP) cm/cm^2 s cmHg), V is the downstream volume in (cm^{-1}), L is the thickness in (cm), T_o & p_o are the standard pressure and temperature respectively, T (K) is the measurement temperature, A is the membrane surface area in (cm^2), Δp is the pressure difference between the feed and permeate side, $(dp/dt)_{ss}$ & $(dp/dt)_{leak}$ are the rates if the pressure rise in the steady state due to the gas permeation & setup leak respectively.

Pure gas selectivity which called ideal selectivity is defined as the ratio of pure gas permeability:

$$\propto_{A/B} = \frac{P_A}{P_B} \quad (9)$$

Where P_A is the permeability of gas A & P_B is the permeability of gas B.

3.5 Mixed Gas Permeation Measurement

In mixed gas condition, a premixed gas was used as a feed gas to the membrane cell and the method used in this case is the constant pressure method. In this technic, the premixed gas is introduced to the membrane film after regulating the feed pressure via pressure regulator, gases at different rates permeate through the membrane thickness and sent to a mass flow meter (MKS M-330, 0 – 1 SCCM) to measure the flow rate and then to micro GC (INFICON 3000 micro GC) to measure the exact compositions for each gas. Permeability and separation factors can be determent based on the flow rate and composition of a certain gas. The reject follow rate is control by mass flow controller (ALICAT SCINTIFIC, 0 – 100 SCCM), the retentate flow rate is adjusted based on the stage cut needed. Both feed and reject stream can be directed to the micro GC to measure the gas concentration.

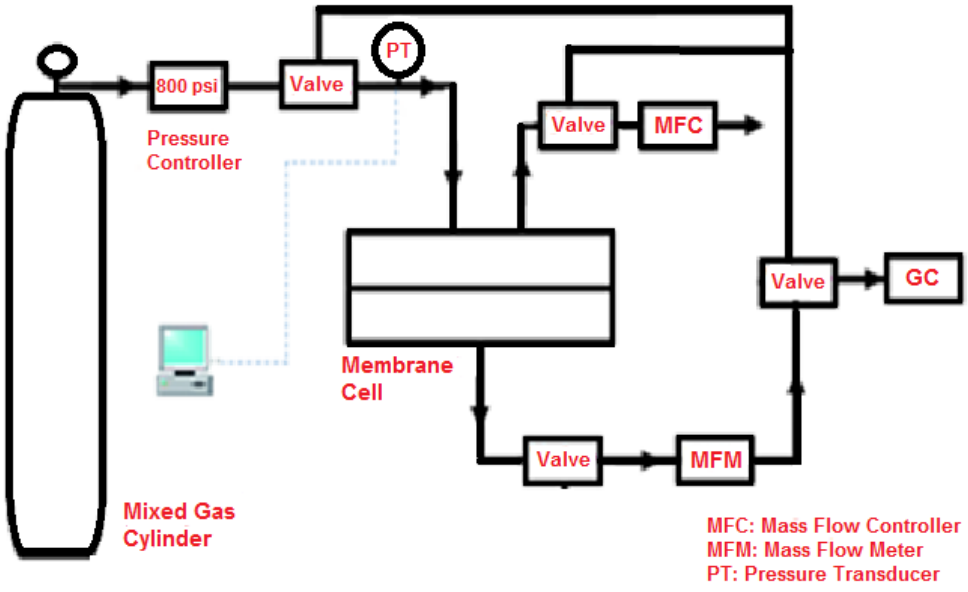


Figure 33 Mixed gas permeation setup.

The permeability calculation for mixed gas condition is different from pure gas as the feed and permeate gas compositions should be taken into account, so the following equation is used:

$$P_i = \frac{y_i Q l}{((\frac{p_{feed}\, x_i + p_{reject}\, z_i}{2}) - p_{permeate} y_i)} \quad (9)$$

Where P_i is the permeability of component I and X_i, Y_i and Z_i are the concentration of the same component of the feed, permeate and reject respectively. Q is the flow rate of the permeate stream in cm^3 STP/s and L is the membrane thickness in cm. P is the pressure for different streams.

The separation factor is calculated as follow:

$$Seperation\ factor = \frac{y_A/y_B}{x_A/x_B} \quad (10)$$

Where Y_A & Y_B are the permeate concentration of gas A and B respectively, whereas, X_A & X_B are the feed concentrations of the same gases.

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Synthesis of PPL and TR-PBI

Synthesis of polypyrrolone (PPL) carried out in multiple steps following the synthesis route explained in Ref. [45]. First, poly(amino amic acid) was formed by reacting stoichiometric amount of aromatic dianhydride (6FDA) and aromatic tetraamine (DAB) monomers through polycondensation reaction. Then, via themal imidization approach, the polyaminoimide (PAI) membranes were obtained after treating them at 250 ^{o}C under vacuum. After that, the thermally rearranged aromatic polybenzimidazolimide (PPL) polymer was synthesized by reheating PAI membranes under vacuum to 300, 350, 400 and 450 ^{O}C. The intent here is to study the relationship between the final treatment temperature, the ring closure and its effect on gas permeation properties.

The aromatic polybenzimidazolimide (PPL) was taking as a precursor polymer to synthesis polybenzimidazole (TR-PBI). The PPL (450) membrane (with full cyclization) was treated by 1 M NaOH solution for further alkaline treatment. During this step, the carbonyl group will open into carboxylic acid and by further thermal treatment at 450 ^{O}C; CO_2 will evolve leaving TR-PBI (450) as the final resultant membrane. Any attempts to treat partially cyclized PPL membrane will result in mechanical collapse as the main chain of PAI will break up during alkaline treatment. The below picture (figure 34) shows a PAI membrane before thermal treatment which has a brown transparent color, while after the thermal treatment at 450 ^{0}C it became an opaque black more fragile membrane. In addition, the radius of the membrane has reduced by one mm during the thermal treatment process.

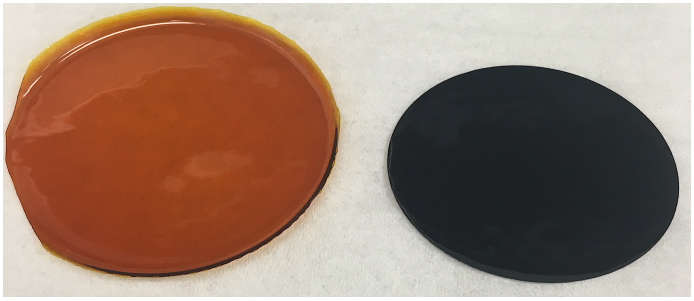


Figure 34 Picture of PAI membrane in the left and PPL (450) membrane at the right.

The FTIR characterization spectrum for both PAI (250) and PPL (450) membranes show -C=O peaks at 1758 cm^{-1} (Fig.35 (a)). Similar absorption bands were detected at 1620 cm^{-1} for PPL (450), iPBI and PBI (450) membranes which indicate –C=N- (Fig. 35 (b)). The N-H bonds for PAI (250) membrane is clearly observed by the wide peak between 3500 and 2600 cm^{-1} (Fig. 35 (d)) as well as the peak at 1640 cm^{-1} (Fig. 35 (c)). For iPBI membrane, the very wide peak between 3700 and 2700 cm^{-1} in addition to the peak at 1400 cm^{-1} are characteristic for -O-H in the carboxylic group, Fig. 35 (e) & (f) respectively.

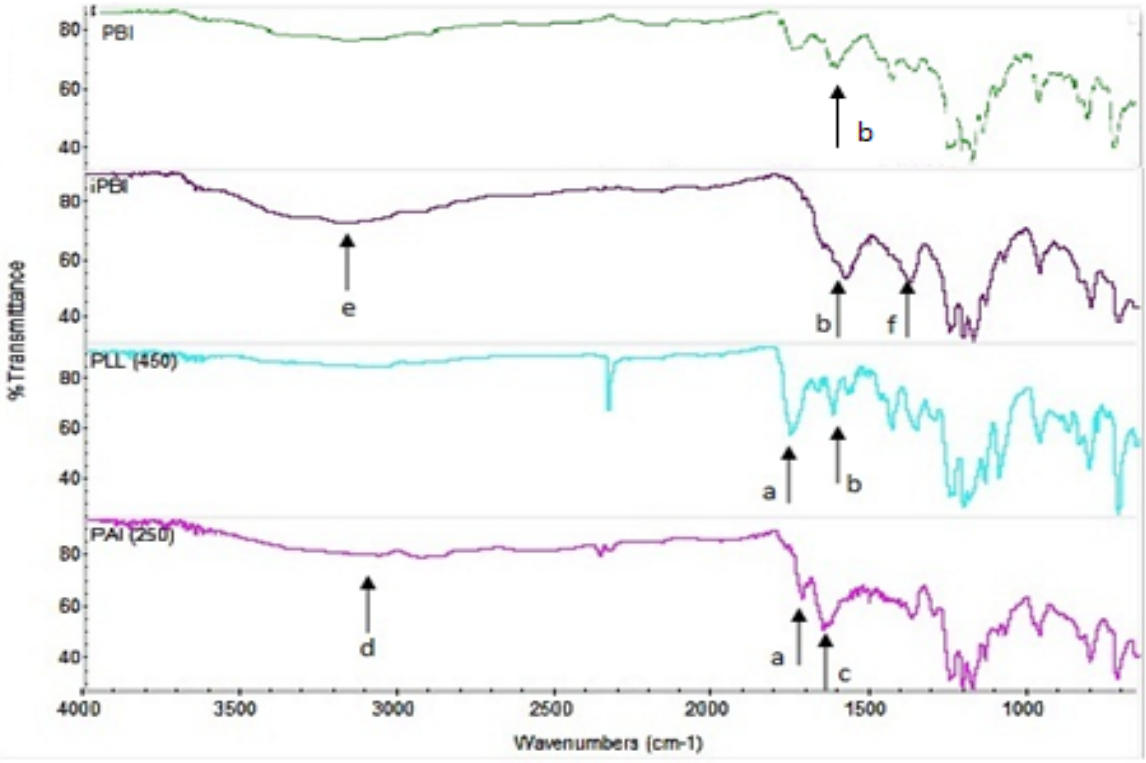


Figure 35 FTIR spectra of PAI (250), PPL (450), iPBI and PBI membranes.

To investigate the thermally stability as well as to support that the thermal reaction took place for precursor membranes, thermo-gravimetric analyses was conducted. As shown in figure 5, PAI (250) membrane experiences a weight loss starting just before 250 ^{o}C and ends 450 ^{o}C which is the range where the thermal reaction occurs (Fig. 36). This weight lost is an evidence for polymer cyclization process where PAI structure loss H_2O and rearrange to PPL structure. Furthermore, the polymer starts to degrade at around 500 ^{o}C leaving only 65% of its weight as residual mass at 600 ^{o}C. On contrary, PPL (450) and PBI membranes exhibit very thermally stable structures as they only lost less than 1% of its original mass at around 550 ^{o}C where they started to degrade. As a result, to this outstanding stability, it is clear that the membranes were already fully cyclized.

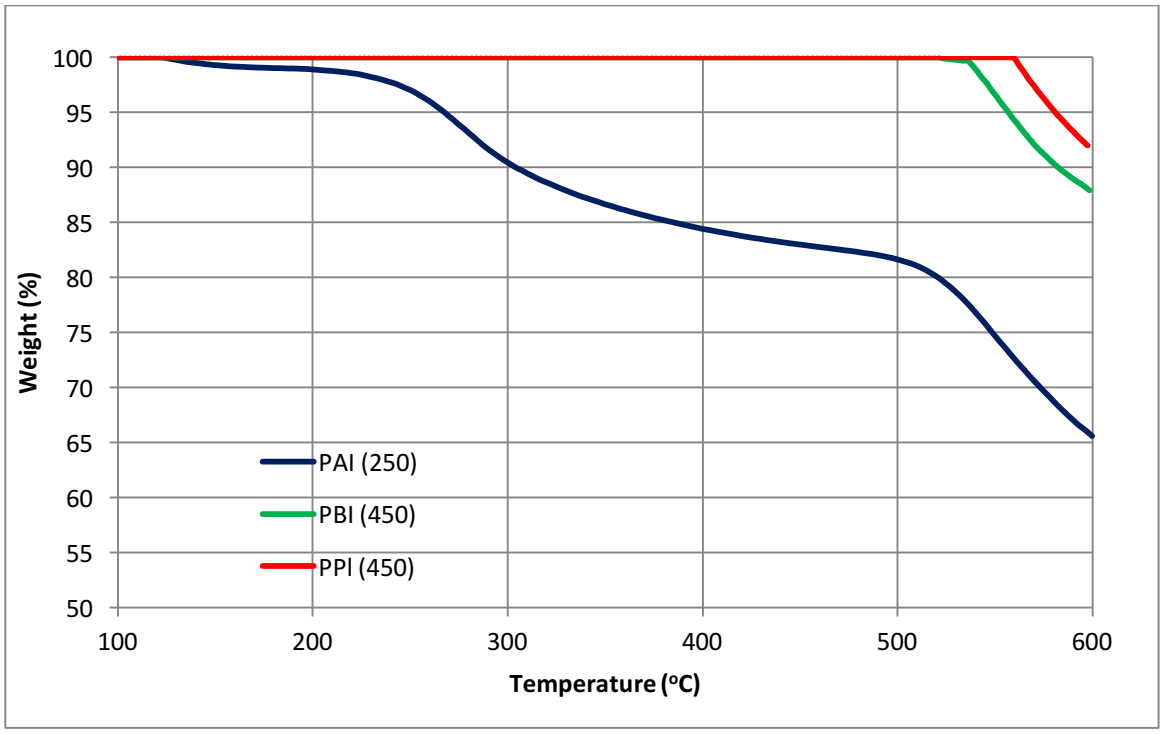


Figure 36 Thermograms of PAI (250), PPL (450) and PBI (450).

4.2 Pure Gas Permeation Result

The dense membranes with thickness of around 100 μm were used to assess the gas permeation properties. All experiments were carried out using pure (single) gases at 100 psia and 25°C. For all membranes, He, CO_2, N_2 and CH_4 gases with purity of 99.9 were tested as a feed gas and for PPL (450) membrane, H_2 and O_2 were additionally tested; all permeability result and ideal selectivity are summarized in table 16. Generally, the permeability of a certain gas increases as the final heat treatment temperature increases, whereas, the ideal selectivity for a pair like He/CH_4 or CO_2/CH_4 decreases. As the temperature of the final treatment increases, higher free volume will be produced due to ring closure which results in a permeability promotion and ideal selectivity reduction. The iPBI intermediate membrane has a very low permeability as well as selectivity for all gases as expected due to the carboxylic group that will add additional interaction between polymer chains resulting in a compacted tight structure. However, the produced PBI membranes were not mechanically strong and usually cracked during the testing. So, no pure gas permeation result was obtained for this type of polymer, however, there is only one data point for mixed gas result and will be shown in the following sections.

Table 16: Permeability and ideal selectivity for PAAc, PAI and PPL membranes for several gases at 100 psia and 25 °C.

Sample		Permeability (Barrer)[a]					
		N_2	CH_4	He	CO_2	O_2	H_2
A	PAAc	0.14	0.078	17.0	4.7	-	-
B	PAI	2.8	1.6	95.4	62.0	-	-
C	PPL (300)	2.3	1.1	109.7	56.9	-	-
D	PPL (350)	4.0	2.0	145.2	84.8	-	-
E	PPL (400)	4.7	2.5	150.0	93.6	-	-
F	PPL (450)	9.5	6.6	220.7	193.7	45	323
G	iPBI	1.5	1.2	54.0	10.6	-	-
H	PBI (450)	-	-	-	-	-	-
Sample		**Selectivity**					
		CO_2/CH_4	He/CH_4	N_2/CH_4	CO_2/N_2	O_2/N_2	H_2/CO_2
A	PAAc	60.4	218.3	1.8	33.6	-	-
B	PAI	39.5	60.8	1.8	22.3	-	-
C	PPL (300)	54.2	104.5	2.1	25.3	-	-
D	PPL (350)	42.4	72.6	2.0	21.2	-	-
E	PPL (400)	37.3	59.8	1.9	20.1	-	-
F	PPL (450)	29.4	33.5	1.6	18.7	4.74	1.7
G	iPBI	9.2	45.0	1.3	7.23	-	-
H	PBI (450)	-	-	-	-	-	-

Figure 37 compares the results of the present study with the pure gases result from previous reported for the same membrane structure (Ref [45]). This work result match with good agreement prior art for the same membrane material, however, there is a slight difference between the two results which seems consistence for each gas that could be due to the accuracy of the measurement method or it might be due to the feed condition as the feed pressure in this study experiments is 100 psi, however, it was not mention in their paper. Since their result slightly higher, most likely they used a feed pressure lower than 100 psi which result in overestimating the permeability of all gases. Figure 38 shows graphically how CO_2 permeability as well as CO_2/CH_4 selectivity changes with thermal treatment where membranes A, B, C, D, E, F, G in x-axis represent PAAC, PAI, PPL (300), (350), (400), (450) and iPBI respectively.

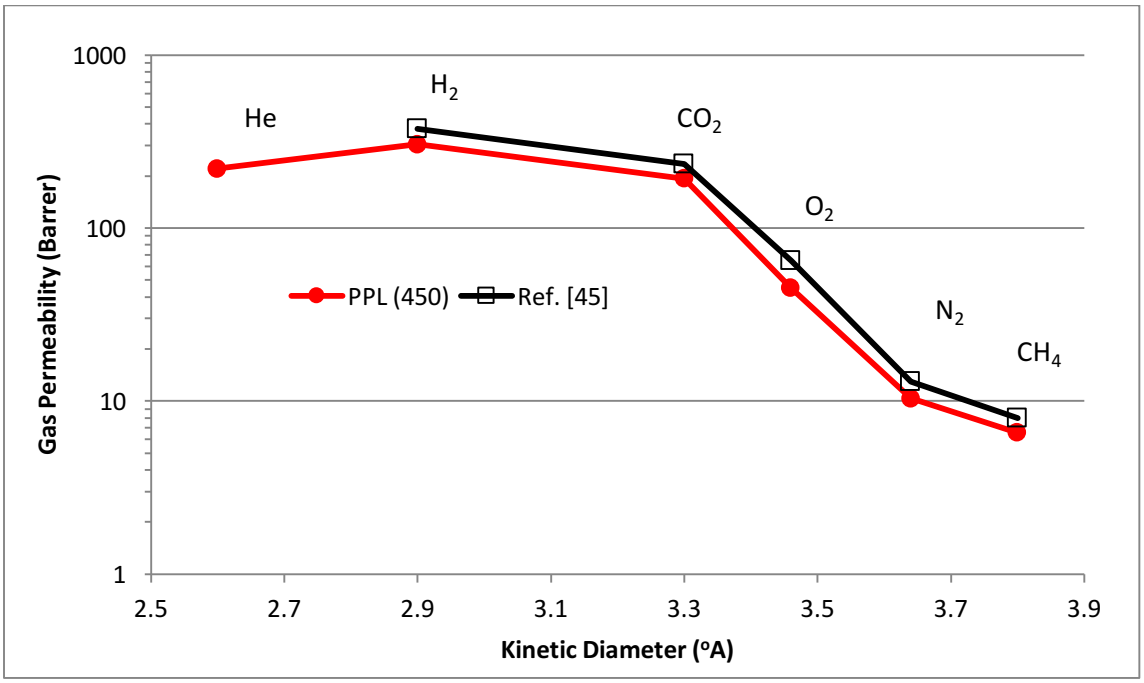


Figure 37 Permeabilities of gas molecules of PPL (450) and TR (450) [45].

The main characteristic that governs the transport phenomena in TR polymer is the micro porosity that result from the thermal reaction which is controlled by the treatments temperature and the time of the exposure to that heat. In other word, the thermal history or the path that has been take has no influence either on the degree of the micro porosity nor the permeation properties of the membrane. In order to approve that, two PAI membranes were treated at different paths: one was treated at 300, 350, 400 and then 450 ^{o}C and the temperature was hold for one hour at each step. However, the other membrane was treated at 450 ^{o}C directly for 2 hours and the gas permeation results were almost the same for both membranes which prove that the path to get certain porosity does not matter as far as you reach to it.

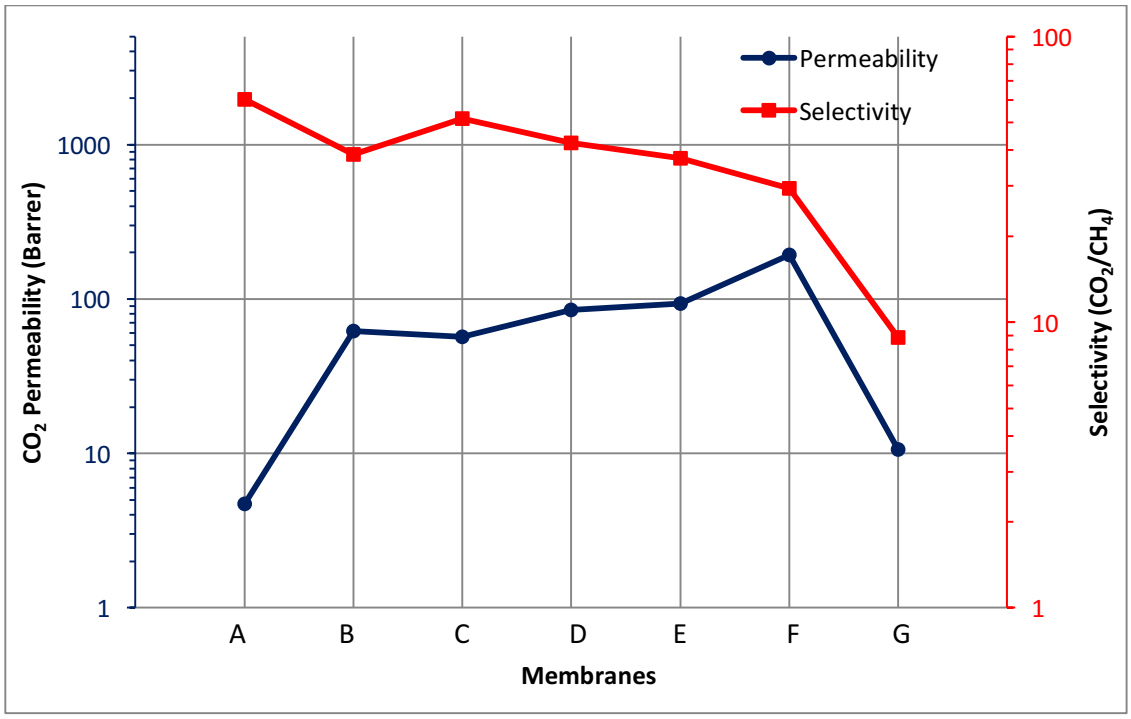


Figure 38 Permeability of CO_2 and CO_2/CH_4 selectivity for different membrane structures.

4.2.1 CO_2/CH_4 Separation

Acid gas removal which is CO_2/CH_4 separation is the main focus of this study and the second most investigated application in gas separation membrane. Pure gas data is considered as good indication of the membrane performance and provides decent starting point. This section will compare PPL membranes with other polymers in literature. So, figure 39 illustrations the CO_2 permeability and selectivity of CO_2/CH_4 pair relationship for different membranes prepared in this study which lay on the 2008 upper limit [53,54]. Also, the figure compares those membranes performance with commercially available polymers like Poly Phenylene Oxide (PPO), polysolfune (PSF) and cellulose acetate (CA). Undoubtedly, PPL membranes have much better permeability and selectivity combination than any commercial polymers [10, 55, 56, 57]. One important fact to keep in mind is that most of reported data that have been used to plot upper bound graph are obtained under low feed pressure condition usually 15 psi which overestimates the membrane performance. However, this study results were acquired at 100 psi and yet it showed a competitive performance.

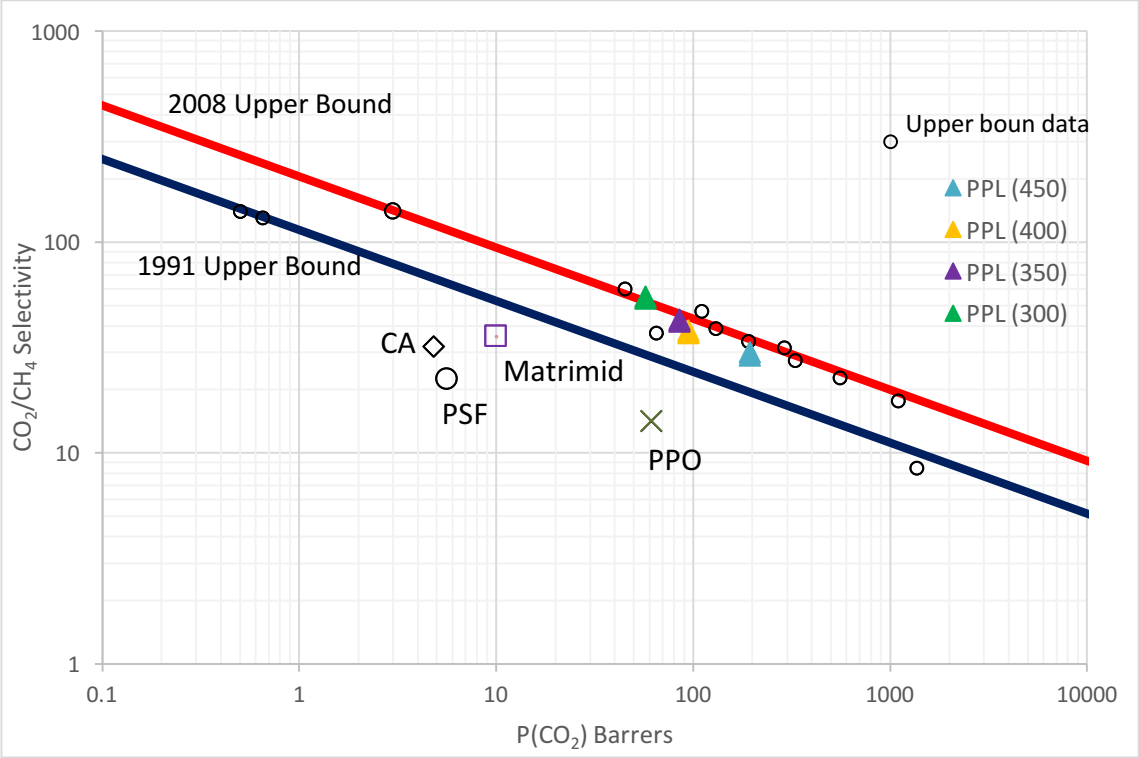


Figure 39 Relationship between gas permeability and selectivity of PPL (450) with upper bounds for CO_2/CH_4 pair. [53]

4.2.2 O_2/N_2 Separation:

Nitrogen enrichment application or in another word O_2/N_2 separation is the most studied pair of gases in the whole membrane gas application. Many industries require high purity of nitrogen such as refrigeration, inerting, enhance oil recovery and electronic industry [6]. Other applications use the oxygen rich stream as a feed to the furnaces instead of air to improve the combustion and bottleneck the size of the furnace.

Although, both O_2 and N_2 are non-condensable gases (compare to CO_2) and plasticization is not an issue for such a separation, but it not easy to separate this pair from each other. The kinetic diameter for O_2 is around 3.46 ^oA, whereas, it is 3.64 ^oA in case of N_2. This small difference in size make it hard to separate by a polymeric membrane and usually the selectivity is below 10. Figure 40 compares the PPL (450) result for air separation application with other polymer membranes including CA, PSF and PPO. PPL (450) showed a moderate performance (as both gases are not condensable, unlike CO_2) which lay on 1991 upper bound, however, it has a better performance than the commercially available polymers [10, 55, 56, 57].

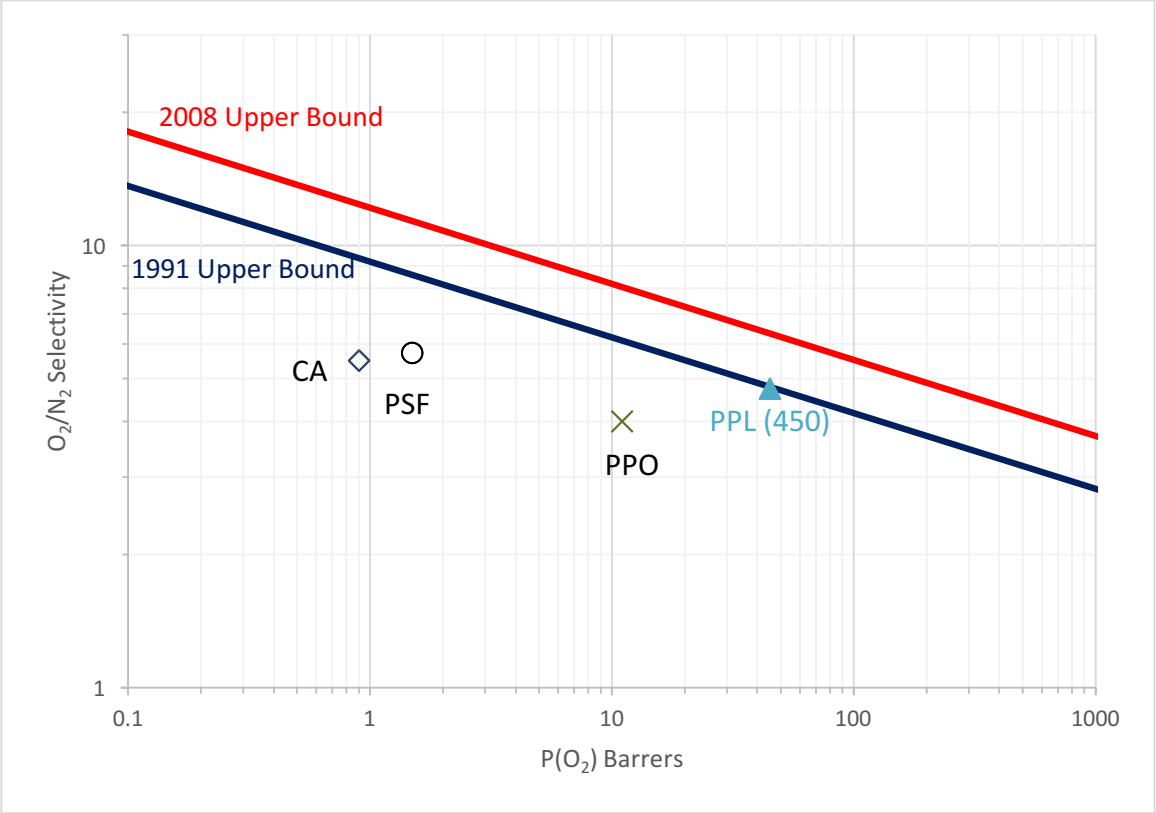


Figure 40 Relationship between gas permeability and selectivity of PPL (450) with upper bounds for O_2/N_2 pair. [53]

4.2.3 H_2/N_2 Separation

Hydrogen separation was one of the first application that was investigated by membrane for gas separation due to its high permeability compare to other gases which lead to high attractive selectivity. For that the first large scale gas separation membrane was hydrogen recovery from ammonia purge gas where nitrogen is reacting with hydrogen over a catalyst. The membrane is used to separate the unreacted hydrogen and recycle it to the main feed as the reaction yield is low.

PPL (450) membrane could be a candidate ammonia purge gas recovery application as it showed good performance in separating H_2 from N_2 which placed PPL (450) in a position that is above 1991 upper bound as showed in Fig. 41.

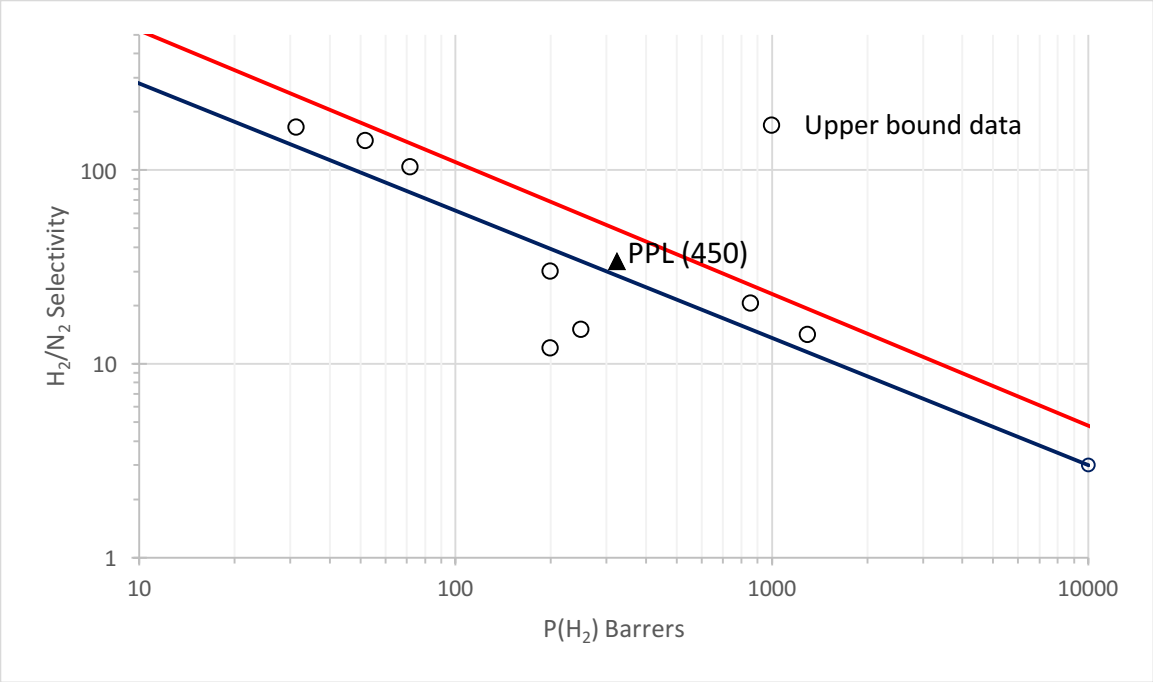


Figure 41 Relationship between gas permeability and selectivity of PPL (450) with upper bounds for H_2/N_2 pair. [53]

4.2.4 H_2/CH_4 Separation

Refinery gas purification application is another example of H_2 separation membrane where H_2 needs to be separated from CH_4. In refineries, the crude oil is separated to many high molecule weight petrochemical products depending on their boiling point, those products usually fed to what is known as cracking units. In the cracking process, high molecular petrochemical feedstocks get broken down (cracked) into smaller and more valuable components. Hydrogen is used in this process to improve the reaction that takes place, for that it is called hydrocracking process. Just like the hydrogen recovery from ammonia purge gas application, polymeric membrane offers a way to recovery the unreacted H2 and recycle it back to feed the hydrocracking unit.

PPL (450) membrane is an excellent choice for this application as hydrogen is highly permeable and has a permeability above 300 Barrer with H_2/CH_4 selectivity around 50 which is suitable for particular application. PPL (450) possess high permeability compares to commercial polymer such as CA, PSF, PPO and Matrimid as shown in Fig. 42 [10, 55, 56, 57].

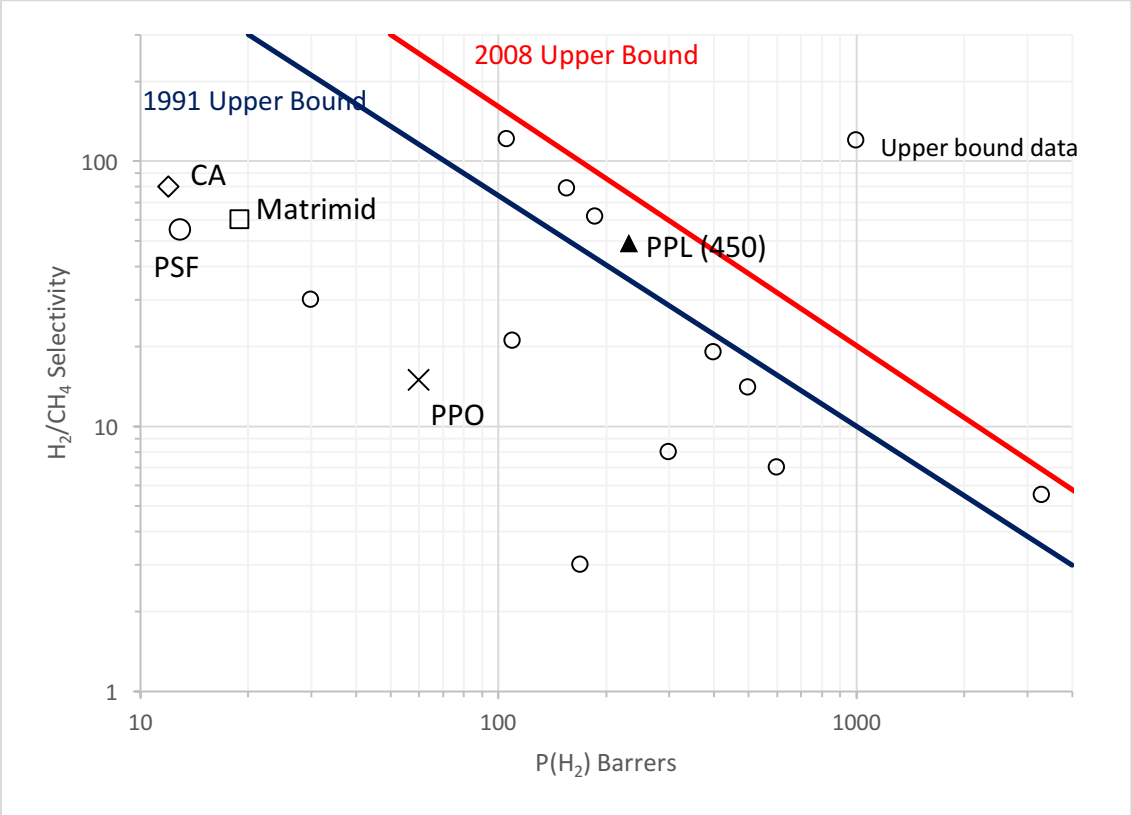


Figure 42 Relationship between gas permeability and selectivity of PPL (450) with upper bounds for H_2/CH_4 pair. [53]

4.3 Mixed Gas Permeation Result

After screening the different membranes using pure gases, PPL (450) membrane was selected to further investigation under mixed gas condition at high pressure. Although, PBI membrane showed a better performance (it was tested under mixed gas condition only), but its weak mechanical strength was a limitation to test under different environments. Therefore, for PPL (450) membrane, different premixed gas feeds were used to study certain phenomena or to target potential applications; hence binary, ternary and quaternary gas mixtures were used. Mixtures of some or all of the following gases were used in the experiments CH_4, CO_2, N_2, He and C_2H_6.

4.3.1 CO_2 Removal from Natural Gas Streams

One main application for gas separation membrane is CO_2 removal from natural gas streams where CO_2 needs to be selectivity separated from a gas mixture contains CH_4, N_2 and some C2+ (heavy hydrocarbons). Although, the gas composition varies from well to well, the CO_2 content usually is not more than 10% [58]. Methane, the main component of natural gas, also vary depending on the well quality, from 60% to 90%. Taking that into consideration, a quaternary gas mixture containing 59% CH_4, 30% N_2, 10% CO_2 and 1% C_2H_6 (with represent a low quality natural gas) has been prepared as a feed gas for studying the permeation properties of the membrane. The effects of the feed pressure and stage cut on the membrane performance have been studied and the results are reported in Figures 7 to 9. Three pressures (400, 600, and 800 pisg) and five stage cuts (1.2, 2.8, 4.2, 6.4, and 9.8%) have been considered.

Generally, it is observed that the permeability of CO_2 slightly decreases from 54 to 50.5 Barrer as the pressure increases from 400 to 800 psig. However, CO_2/CH_4 permeability ratio is observed to be almost constant around 45 (Fig. 44). As a result of the pressure increase, large force is applied on the membrane surface. This force compresses the polymer molecules and reduces the free volume. Consequently, the permeability, which directly depends on the free volume, decreases. On the other hand, the partial pressure of CO_2 will increase as the total pressure increases resulting in slight increase of permeability. The two effects counteract each other, which explain the constant permeability (with little decrease within experimental errors). However, this is not usually the case, with other membrane materials, it is reported in the literature that many polymeric membranes lose their selectivity at elevated pressures in presence of condensable gases like CO_2 [60-62]. The main reason for this drop-in selectivity is attributed to the plasticizing effect of CO_2 on polymer membrane as it causes swelling to the polymer matrix (will be discussed in more details in coming sections). Furthermore, generally CO_2 permeability drops down to a minimum value as feed pressure increase, then starts to increase sharply, this critical pressure (where permeability reaches its minimum) is known as plasticization pressure (Fig. 43) [63]. One possible explanation for the permeability decline at the begging is the competitive sorption as the sorption in glassy polymers follows the dual-mode theory. This theory declares that there are two mechanisms for gas sorption into polymer matrix which are Henry's law and Langmuir mode. Langmuir mode suggests the existence of fixed finite number of Langmuir sites (frozen micro-voids) due to the non-equilibrium nature of glassy polymers. Consequently, in case of mixed gas feed, there is a competition between several gases to fill those sites which results in a lower permeability. Consequently, as PPL (450) membrane does not show any sign of neither selectivity decline nor permeability

increase, it can be concluded with confident that this material has strong resistivity to plasticization [4].

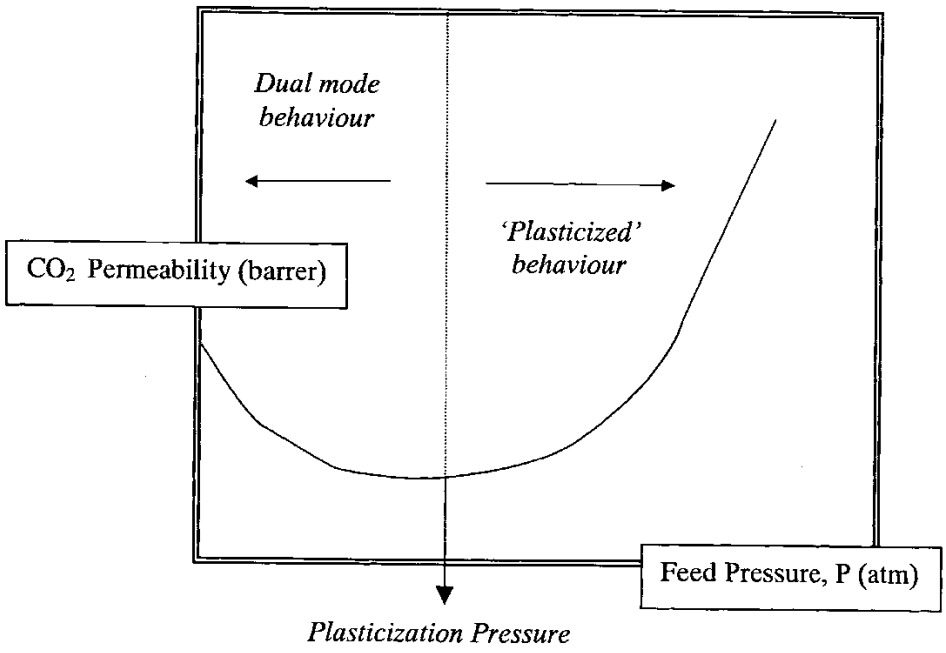


Figure 43 Generic permeation behavior of glassy polymers. [4]

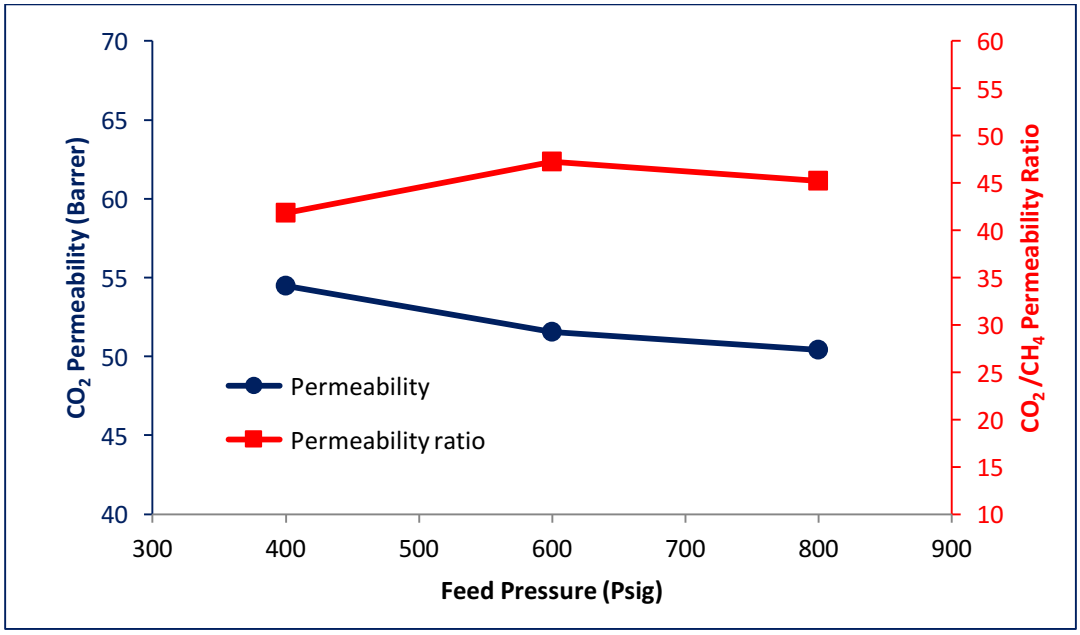


Figure 44 CO_2 permeability and CO_2/CH_4permeability ratio of PPL (450) membrane under quaternary gas mixture at different feed pressures.

In mixed gas feed condition, besides the membrane selectivity, the total pressure ratio ($p_{feed}/p_{permeate}$) is an important factor to be considered in the process [64]. Conducting an experiment with a pressure ratio less than the intrinsic membrane selectivity, will lead to lower performance of the membrane. Similarly, having low selective membrane while working with high pressure ratio is unnecessary additional cost as the overall process selectivity will be govern by selectivity of the membrane. In order to study the effect of the total pressure ratio, both the separation performance and the concentration of the CO_2 in permeate stream have been measured with respect to the total pressure ratio (Fig. 45). According to Figure 45, higher pressure ratio enables better performance of the membrane, manifested in higher separation factor of CO_2/CH_4 with better CO_2 concentration in the permeate side. At a total pressure ratio of 53 (CO_2 partial pressure is 6.8 in this case) and a separation factor of 33, the CO_2 concentration has increased from 10% in the feed to almost 80% in permeate side.

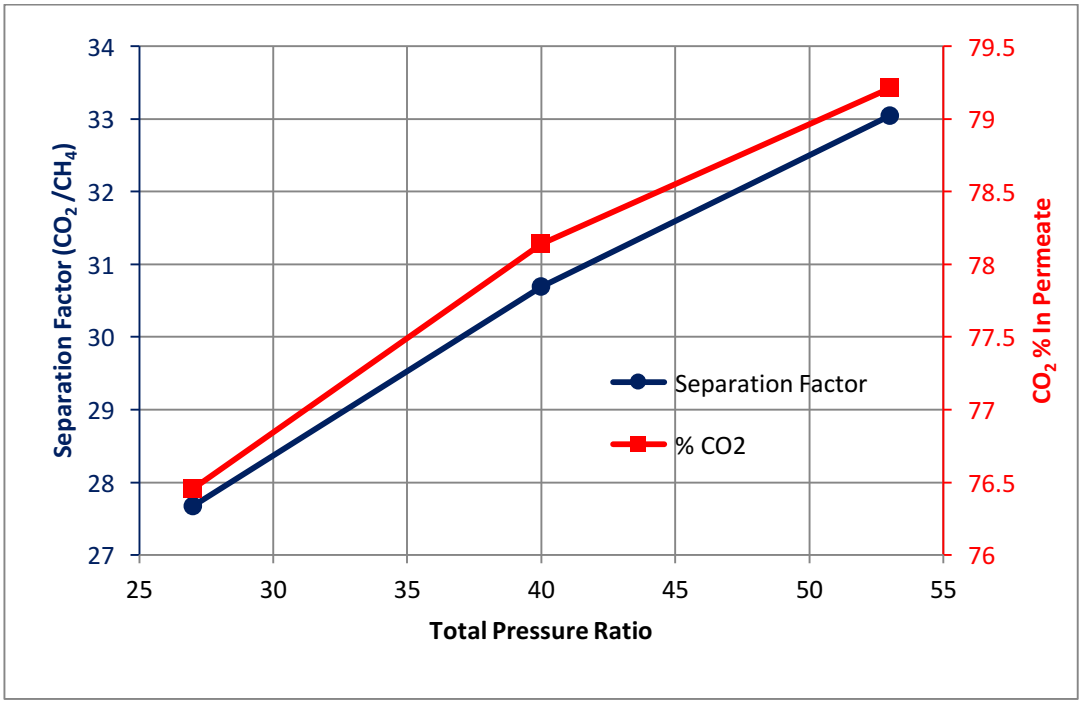


Figure 45 CO_2/CH_4 separation factor and CO_2 percentage in permeate stream for PPL (450) membrane under quaternary gas mixture at different pressure ratios.

In industry, the total cost of the CO_2 removal is determined by adding the operational cost to the CH_4 loses during the operation. Typically, in industry the situation is as follow, the feed gas has a fixed flow rate which contain certain amount of CO_2 that need to be removed so the membrane based process need to be designed accordingly. By increasing the membrane surface area, the permeate flow rate will increase which contains CO_2 resulting in higher CO_2 removal. The ratio of permeate flow rate to feed flow rate is called stage cut, higher stage cut requires higher surface area (additional cost) resulting in more CO_2 being removed (advantage), on the other hand, more CH_4 will be lost (disadvantage). In lab scale experiment, the membrane surface area is limited by the size of the cell, therefore, in order to increase stage-cut, feed flow rate must be reduced which can be achieved by reducing reject flow rate. Two important points to highlight here, first the reject stream composition must be monitored and any variation should be included in the calculation, second, increasing stage-cut to high may result to unperfected mixing and the membrane may start to see different gas composition than the actual feed and that is the reason why the stage-cut was limited to 10% as will be shown later. So far, all experiments were conducted at around 1% stage-cut to study the membrane gas permeation properties. At this stage-cut only 10% of the CO_2 was removed from the feed. In order to determine the effect of stage-cut on the membrane's performance, other experiments were conducted at 800 psig using various stage-cuts by changing the reject flow rate. According to Fig. 46, as the stage-cut increased, the percentage of CO_2, removed from the feed stream, significantly increased. PPL (450) membrane has outstanding removal rate as it can remove 80% of CO_2 with 10% stage cut only which reflect the membrane surface area needed in real industrial application where the feed flow rate is fixed and the surface area has to be increased to achieve the desired CO_2 removal. In addition, CO_2/CH_4 permeability ratio was improved up to the stage-cut of 3 beyond which it stabilized at the value of 55. At higher stage cuts, other gases start to have more chance to permeate through the membrane thickness because the reject flow rate has been reduced which provide more time for less selective gases to permeate. The same logic applies when designing industrial membrane module where the stage cut can be increased by increasing the surface area which allows low permeable gases to permeate through the membrane. That being said, even at 10% stage cut, the CH_4 loses is less than 2.5% which is another very critical parameter in industrial application. So, while trying to remove as much CO_2 as possible, it is crucial to minimize the CH_4 slippage to make the whole process economically attractive. Figure 47, presents the CH_4 loses as a function of the stage cut, looking at figure 46 and 47 together illustrate the need to optimize the membrane process to achieve feasible design.

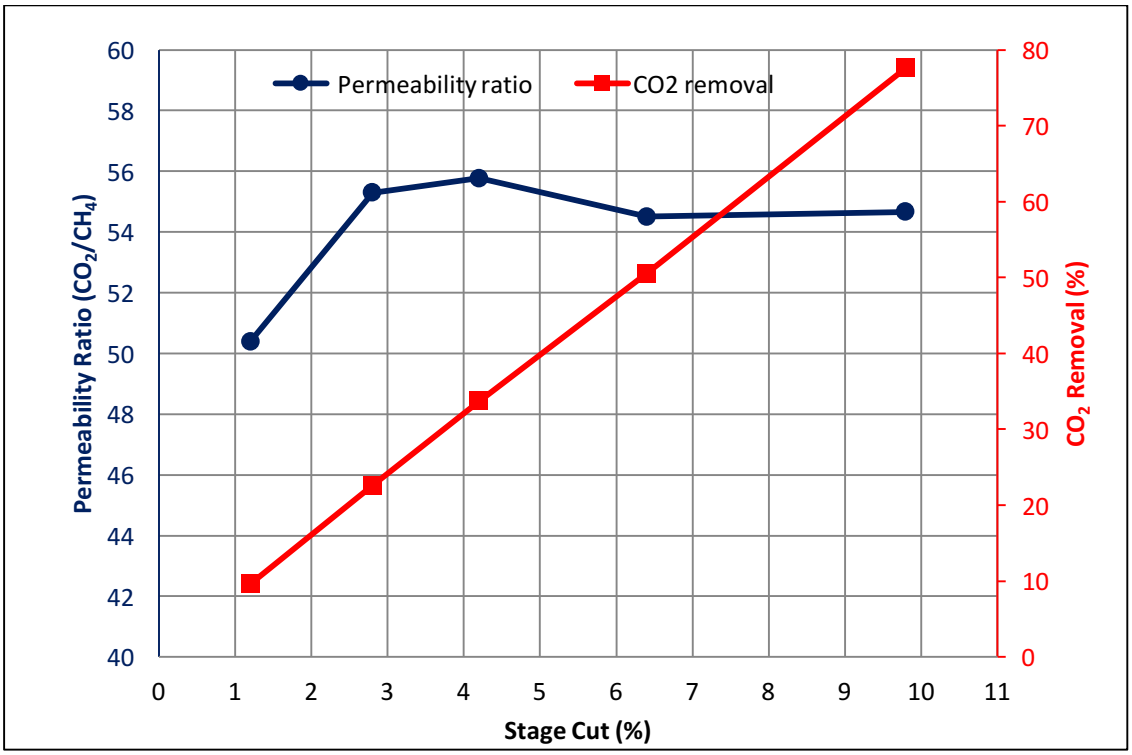


Figure 46 CO_2/CH_4 permeability ratio and CO_2 removal levels for PPL (450) membrane under quaternary gas mixture at various stage cuts.

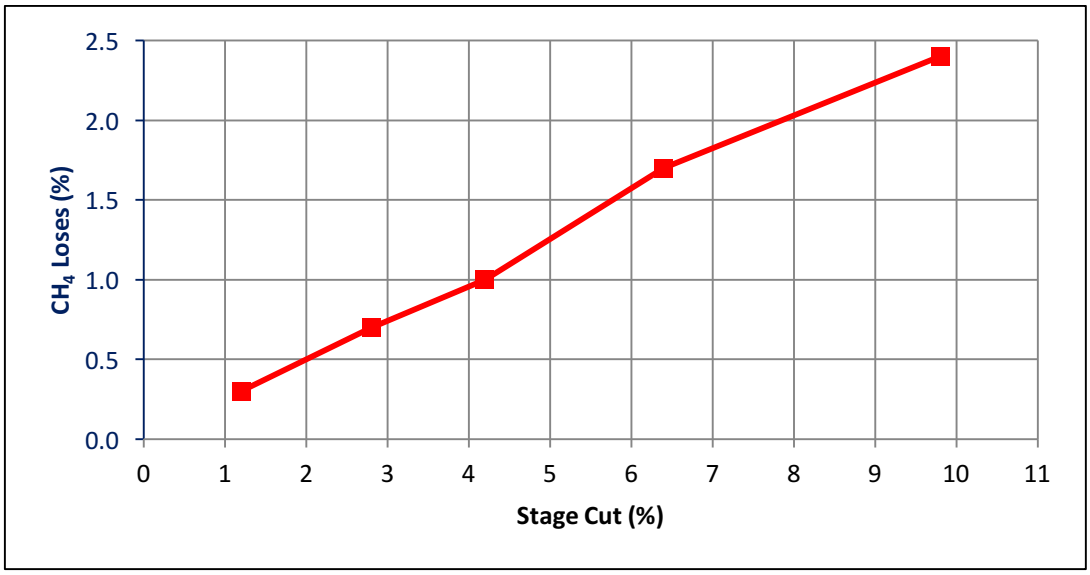


Figure 47 CH_4 loses for PPL (450) membrane under quaternary gas mixture (10% CO_2, 59% CH_4, 30% N_2 and 1% C_2H_8) at various stage cuts.

Polybenzimidazole (PBI) membranes (the second thermally rearranged membrane in the proposal) were not mechanically strong and they cracked several times during gas permeation testing. Hence, no pure gas permeation result was obtained for this type of polymer, however, only one data point was measured which was under quaternary gas mixture (10% CO_2, 59% CH_4, 30% N_2 and 1% C_2H_8) at 200 psig feed gas pressure (the membrane got cracked when the pressure increased to 400 psig). The PBI membrane showed an outstanding performance with extremely high permeability-selectivity combination which place it away above the 2008 upper bound. Although the upper bound is for pure gas experiment results, but it is still good comparison as it expected to have even better performance in case of pure gas condition (as most of the membrane material). Moreover, figure 48 showed the up normal gas permeation properties of PBI (450) membrane with comparison to PPL (450) (at 400 psig) result with was reported in pervious section.

The reason of presenting this single data point is to draw the attention to the fact that having high selective and permeable membrane is not enough as it should be mechanical strong to handle the feed pressure. That explains why there are so many membrane materials that have been tested for gas separation application yet only a few materials made it to industry.

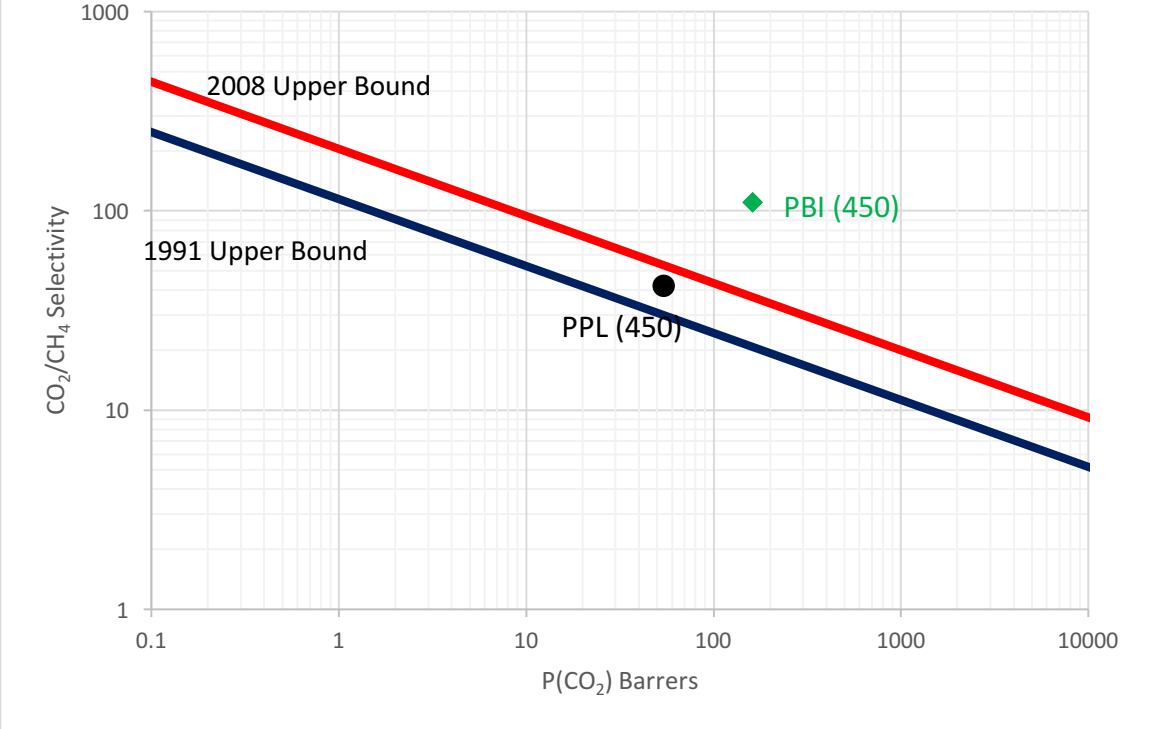


Figure 48 PBI (450) & PPL (450) membranes performance under quaternary gas mixture (10% CO_2, 59% CH_4, 30% N_2 and 1% C_2H_8) at 200 and 400 psig respectively.

4.3.2 Helium Recovery from Natural Gas Streams

Helium exists in natural gas streams in small and very dilute concentration which make it hard and sometimes uneconomical to recover it using the conventional technologies. Membranes with high selectivity toward helium could be a good candidate to be used as an enrichment step before the conventional process to make the whole process economically feasible. Thus, to study the ability of PPL (450) membrane to recover helium, a feed mixed gas contains 0.14% Helium, 71% CH_4 and 29% of N_2 was introduced to the membrane cell. The feed gas is free of CO_2 because the Helium recovery unit usually comes after the gas treatment unit where CO_2 and H_2S are removed which enrich Helium concentration. Assuming that CO_2 is removed by other technology and not by this membrane, otherwise it will be difficult to separate CO_2 and Helium as they permeate fast through PPL (450) membrane. Hence, an experiment was carried out at two different pressures 400 and 800 psig at 2% stage cut. At 400 psig, Helium permeability was 130 Barrer with He/CH_4 permeability ratio of 49. Doubling the feed pressure results in 30% drop in the permeability as well as slight decrease in the permeability ratio as shown in Fig. 49. The reason for this decline is due to the compression effect and the competitive sorption as helium loses few of the Langmuir sites to the more condensable CH_4 gas. Using the PPL (450) membrane, helium concentration is enriched from 1400 ppm to 20,000 ppm at the low-pressure side with 1.8 stage cut. Furthermore, by increasing the stage cut to 5% the recovery level of helium increased from 31% to more than 80%, however, as expected that is associated with higher CH_4 loses (from 1.4 to 3.9%) as figure 50 illustrates. The same conclusion is obtained as in case of CO_2 removal, allowing for higher stage cuts will result in higher removal/recovery of the targeted more selectivity gas, consequently, more CH_4 will be lost (in this case it is less than 5%).

Table 17 Helium permeability and He/CH4permeability ratio of PPL (450) membrane under ternary gas mixture at 400 and 800 psig.

Feed Pressure	He Permeability (Barrer)	He/CH_4 Permeability Ratio
400 psig	130	49.21
800 psig	101	46.64

Table 18 Helium recovery and CH_4 loses of PPL (450) membrane under ternary gas mixture (71% CH_4, 29% N_2 and 0.14% He) at different stage cuts.

Stage Cut	He Recovery (%)	CH_4 Loses (%)
1.8	31	1.4
5.1	82	3.9

4.3.3 Plasticization effect

Many polymeric membranes plasticized when exposed to condensable gases such as CO_2 at elevated pressure which directly related to the polymer capacity to adsorb penetrant molecules [4]. This physical phenomenon negatively affects the membrane performance as the membrane losses its separation ability due to the swelling of the polymer matrix which allows more gases to penetrate unselectively. Many polymeric membranes plasticized and lose their selectivity, figure 49 show an example taking from reference [65] where 6FDA polyimide based material shows weak resistivity to plasticization at elevated pressure.

A binary mixed gas with 50% CO_2 and 50% CH_4 was introduced to PPL (450) membrane to study its resistivity to plasticization. Figure 50 shows and compares PPL (450) membrane resistivity with other some polymeric membranes such as cellulose acetate, blends of Matrimid with a polyimide P84 (P84/Matrimid) as well as Matrimid with polyethersulfone (PES/Matrimid) [5]. PPL (450) possess an outstanding CO_2 plasticization resistivity as it shows slight increase of CO_2/CH_4 permeability ratio with increasing feed pressure. On the other hand, the other three membranes undergo a continuous decrease in their permeability ratio [5]. Those membrane materials interact more with CO_2 (high affinity to CO_2) causing the polymer matrix to swell, open up and losses its separation ability due to the excessive sorption as a result of high partial pressure of CO_2. Additionally, in case of plasticization, the agitation motion of the polymer chain is enhanced leading to an increase in the permeability of all gases. Oppositely, CO_2 permeability remained constant with little decline giving additional prove of the outstanding resistivity of PPL (450) membrane.

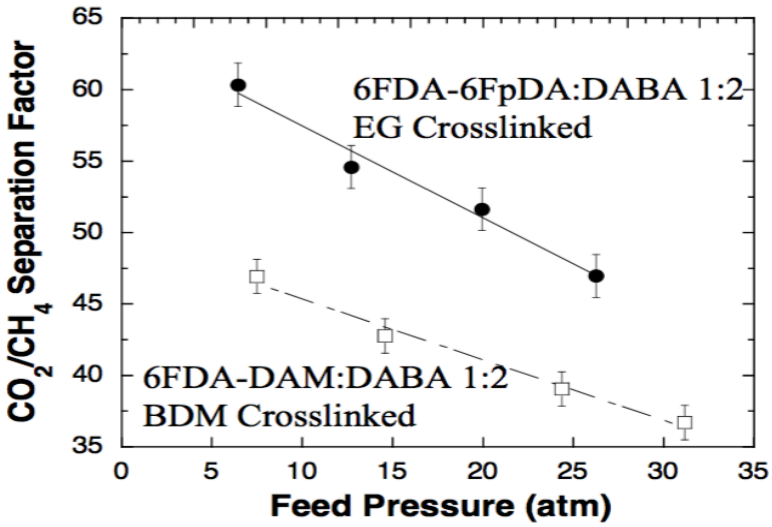


Figure 49 Mixed gas CO_2 permeation and separation factor isotherms with 50/50 CO_2 /CH_4 at 35 ◦ C for 6FDA-DAM:DABA 1:2 benzenedimethanol monoester and 6FDA-6FpDA:DABA 1:2 ethylene glycol monoester. [65]

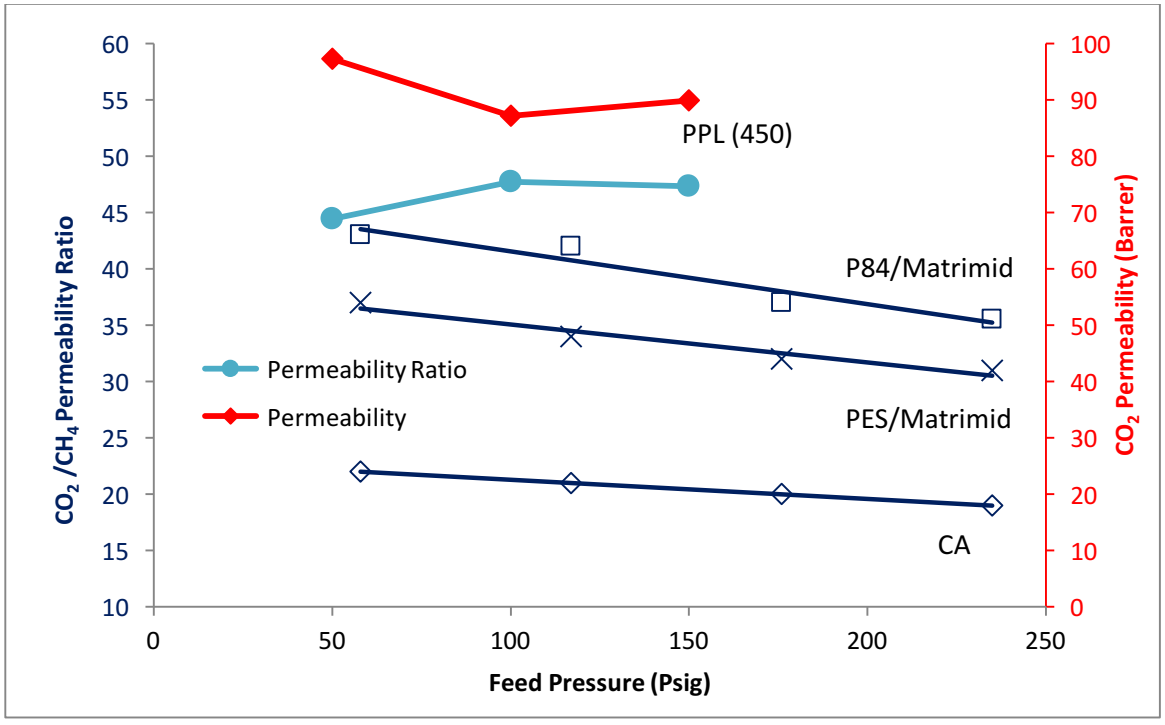


Figure 50 CO_2 permeability and CO_2/CH_4 permeability ratio of PPL (450), CA, P84/Matrimid and PSE/Matrimid membranes under 50/50 CO_2-CH_4 mixed gas feed at different pressures. [5]

To make a better comparison, PPL (450) membrane performance under the quaternary mixed gas was compared with a literature result for a block 6FDA based co-polyimide tested under the same mixed gas composition. From Ref. [60], a co-polyimide (6FDA-mPDA) - (6FDA-durene) membrane with block ratio of (15,000/15,000) has excellent CO_2/CH_4 selectivity under pure gas condition around 37, however, when the membrane was exposed to a similar condition as this study experiment condition (mixed gas at high pressure), the permeability ratio has dropped dramatically. Figure 51 shows how the CO_2/CH_4 permeability ratio dropped sharply by around 50% as the pressure increases from 300 to 500 psig. On contrary, PPL (450) membrane has a CO_2/CH_4 permeability ratio that is more than four time higher and more importantly the ratio stays almost constant up to 800 psig. Both membranes possess similar trend for CO_2 permeability, nevertheless PPL (450) membrane has much higher permeability. So, it is clear that PPL (450) membrane has excellent mechanical strength as well as plasticization resistivity.

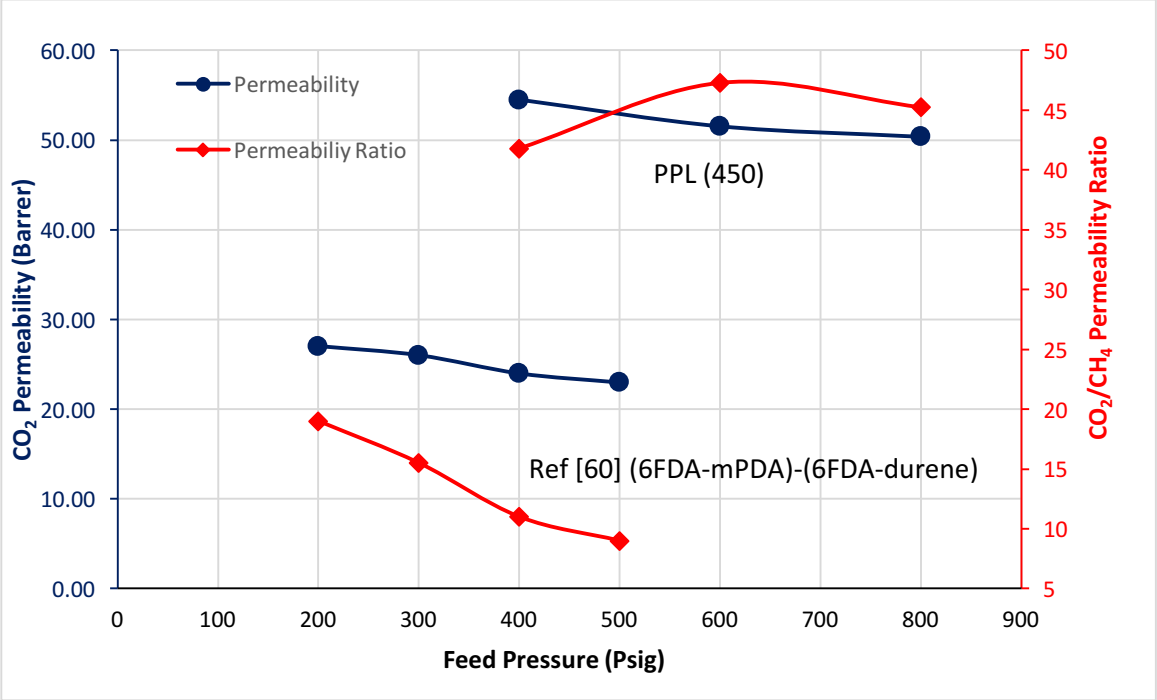


Figure 51 CO_2 permeability and CO_2/CH_4 permeability ratio of PPL (450) and (6FDA-mPDA)-(6FDA-durene) membrane under quaternary mixed gas feed [60].

CHAPTER 5

CONCLUSION & FUTURE WORK

To sum up, polypyrrolone membrane was successfully produced from poly(amino amic acid) (PAAc) at different heat treatment temperatures (300 – 450 ^{o}C) with outstanding thermal stability. In addition, pure gas permeation properties were investigated for multiple gas pairs and PPL (450) displayed excellent transport performance for pair like CO_2/CH_4. Accordingly, PPL (450) membrane was selected for further investigation for natural gas separation application, namely acid gas removal and Helium recovery. The membrane was exposed to various gas mixtures under high feed pressure (800 psig) to study its separation ability under such a harsh environment to simulate the real industrial condition. Remarkably, PPL (450) membrane did not show any sign of plasticization and it was able to remove 80% of the CO_2 in the feed with 10% stage cut by enriching the CO_2 concentration from 10% in the feed to 80% in the permeate stream. Although, CO_2 permeability has decreased in mixed gas condition (compare to pure gas condition) due to competitive sorption, but the CO_2/CH_4 permeability ratio has increased. Moreover, the membrane successfully recovered Helium at very dilute concentration (0.14%) and enriched it to 2% with a recovery level of 80% with only 5% stage cut.

This study has demonstrated the potential of using PPL (450) membrane for natural gas separation applications. Nonetheless, there is still more work needs to be done for this membrane to reach the industrial deployment and it can be summarized in the following points:

a. Developing composite membrane by coating the membrane on top of a compatible support to enhance its mechanical strength.
b. Manufacturing follow fiber module and studying its mechanical properties.
c. Optimizing the productivity (flux) of the follow fibers by reducing membrane thickness without comprising the membrane performance.
d. Investigating the scalability of this type of membrane.
e. Studying membrane resistivity to water vapor and to the chemicals that are usually exist in natural gas streams (BTEX, hydrate inhibitor …) and propose the required pretreatment units.

References

[1] R. W. Baker, "Future Directions of Membrane Gas Separation Technology", *Ind. Eng. Chem. Res.*, Vol.41, (2002), P.1393-1411.

[2] R. W. Baker, "Natural Gas Processing with Membranes: An Overview", *Ind. Eng. Chem*, (2008), P.2109-2121.

[3] R. W. Baker, *"*MEMBRANE TECHNOLOGY AND APPLICATIONS*"*.

[4] S. Kanehashi and K. Nagai, "Analysis of dual mode model parameters for gas sorption in glassy polymers". *Journal of Membrane Science*, Vol.253, (2005), P. 117-138.

[5] T. Visser and N. Masetto, "Materials dependence of mixed gas plasticization behavior in asymmetric membranes" *Journal of Membrane Science*,Vol.306, (2007), P.16-28.

[6] D. F. Sanders and Z. P. Smith, "Energy-efficient polymeric gas separation membranes for a sustainable future: A review", *Polymer* , Vol.54, (2013), P-4729-761.

[7] R. H. Norman and D. R. Paul, "Carbon dioxide plasticization and conditioning effects in thick vs. thin glassy polymer films", *Polymer*, Vol.52, (2011), P-1619-1627.

[8] A.C. Puleo and D. R. Paul, "The effect of degree of acetylation on gas sorption and transport behavior in cellulose acetate", *Journal of Membrane Science*, Vol.47, (1989), P-301-332.

[9] M.D. Donohue, "Permeation behavior of carbon dioxide-methane mixtures in cellulose acetate membranes", *Journal of Membrane Science*, Vol.42, (1989), P-197-214.

[10] Z. Pientka, "Synthesis and Characterization of Polybenzoxazinone and its Prepolymer Using Gas Separation", *Macromolecular Chemistry and Physics*, (2013), P-2867-2874.

[11] Y. M. Lee, "*Patent* No. US 2012/0042777", (2012).

[12] Y. Yampolskii, "Materials Science for Gas and Vapor Separation*",* (2006), England: John Wiley & Sons.

[13] M. Miki, “Synthsis and gas transport properties of hyperbranched polyimide-silica hybrid/composite membrane”, *Polymer,* Vol.5, (2013), P.1362-1379.

[14] K. Okamoto and K. Tanaka, “Gas permeability and permselectivity of polyimides prepared from 4,4-diaminotriphenylamine”, *Polymer*, Vol.24, (1992), P.452-457.

[15] C. A. Scholes and G. W. Stevens, “Membrane gas separation applications in natural gas processing”, *Fuel*, Vol.96, (2012), P.15-28.

[16] T. Y. Suzuki, “Physical and gas transport properties of hyperbranched polyimide–silica hybrid membranes”, *Membrane Separation*, Vol.37, (2012), P.304-311.

[17] I. Pinnau and B. Freeman, “Gas and transport properties of perfluoropolymers”, (2006), *John Wiley & Sons*.

[18] F. Hamad and T. Matsuura, “Performance of gas separation membranes made from sulfonated brominated high molecular weight poly (2,4-dimethyl-l,6-phenyIene oxide). *Journal of Membrane Science”*, Vol.253, (2005), P.183-189.

[19] S. Sridhar and B. Smitha, “Modified poly(phenylene oxide) membranes for the separation of carbon dioxide from methane”, *Journal of Membrane Science* , Vol.280, (2006), P.202-209.

[20] B. Freeman, “*Patent No. 2012/167114A2.* US” (2012).

[21] H. B. Parka, “Thermally rearranged (TR) polymer membranes for CO2 separation. *Journal of Membrane Science”*, (2010), P.22-24.

[22] Z. P. Smith and D. F. Sanders, “Gas sorption and characterization of thermally rearranged polyimides based on 3,3-dihydroxy-4,4-diamino-biphenyl (HAB) and 2,2-bis-(3,4-dicarboxyphenyl) hexafluoropropane dianhydride (6FDA)”, *Journal of Membrane Science* , Vol.415, (2012), P.558-567.

[23] R. Swaidan, B. S. “Pure and mixed-gas CO2/CH4 separation properties of PIM-1 and an amidoxime-functionalized PIM-1”, *Journal of Membrane Science*, (2010), P.95-102.

[24] T. S. Chung and L. Y. Jiang "Mixed matrix membranes (MMMs) comprising organic polymers with dispersed inorganic fillers for gas separation", *Progress In Polymer Science* , 2007,P.483-507.

[25] D. Zhao and J. Ren, "Gas separation properties of poly(amide-6-b-ethyleneoxide)/amino modified multi-walled carbon nanotubes mixed matrix membranes", *Journal of Membrane Science* , Vol.467, (2014), P.41-47.

[26] C. V. Funk and D. R. Lloyd, " Zeolite-filled microporous mixed matrix (ZeoTIPS) membranes: Prediction of gas separation performance" *Journal Membrane Science*, Vol.313, (2008), P.224-231.

[27] X. Ning, W. J. Koros, "Carbon molecular sieve membranes derived from Matrimi polyimide for nitrogen/methane separation. *Carbon*, Vol.66, (2014), P.511-522.

[28] P.S. Tin and T. S. Chung, "Effects of cross-linking modification on gas separation performance on Matrimid membranes", *Journal of Membrane Science*, Vol.225, (2003), P.77-90.

[29] R. Wang and C. Cao, "A critical review on diffusivity and the characterization of diffusivity of 6FDA-6FpDA polyimide membranes for gas separation", *Journal of Membrane Science*, Vol.198, (2002), P.259-271.

[30] Y. Jiang and F. T. Willmore, "Cavity size, sorption and transport characteristics of thermally rearranged (TR) polymers", *Polymer*, Vol.52, (2011), P.2244-2254.

[31] S. Kim and Y. M. Lee, "Rigid and microporous polymers for gas separation membrane", *Progress in Polymer Science*, Vol.43, (2015), P.1-32.

[32] N.B. McKeown and P.M. Budd, "Polymers of intrinsic microporosity (PIMs): Organic materials for membrane separations, heterogeneous catalysis and hydrogen storage", *Chemical Society Reviews*, (2006), P.675-683.

[33] H. B. Park and S. H. Han, "Thermally rearranged (TR) polymer membranes for CO2 separation", *Journal of Membrane Science*, Vol.359, (2010), P.11-24.

[34] J. H. Hodgkin and B. N. Dao, "Thermal conversion of hydroxy-containing polyimides to polybenzoxazoles. Does this reaction really occur?", *European Polymer Journal*, Vol.45, (2009), P.3081-3092.

[35] H. Wang and S. Liu, "The evolution of poly(hydroxyamide amic acid) to poly(benzoxazole) via stepwise thermal cyclization: Structural changes and gas transport properties", *Polymer*, Vol.52, (2011), P.5127-5138.

[36] D. F. Sanders, "Influence of polyimide precursor synthesis route and ortho-position functional groupon thermally rearranged (TR) polymer properties:Pure gas permeability and selectivity" *Journal of Membrane Science*, (2014), P.73-81.

[37] H. SH, "Thermallyrearranged (TR) polybenzoxazole: effects of diverse imidization routes on physical properties and gas transport behaviors", *Macro Molecules*, (2010).

[38] R. Guo , "Synthesis and characterization of thermally rearranged (TR) polymers:effect of glass transition temperature of aromatic poly (hydroxy-imide) precursors on TR process and gas permeation properties", *Journal of Materials Chemistry*, (2013).

[39] D. F. Sanders and Z. P. Smith, "Gas permeability, diffusivity, and free volume of thermally rearranged polymers based on 3,3-dihydroxy-4,4-diamino-biphenyl (HAB) and 2,2-bis-(3,4-dicarboxyphenyl) hexafluoropropane dianhydride (6FDA)", *Journal of Membrane Science*, Vol.409, (2012), P.232-241.

[40] W. Liu and W. Xie, "Acetate-functional thermally rearranged polyimides based on 2,2-bis (3-amino-4-hydroxy-phenyl) hexafluoropropane (APAF) and various dianhydrides for gas separations", Industrial & *Engineering Chemistry Research*, Vol.53, (2014), P.871-879.

[41] Y. F. Yeong and H. Wang, "Thermal induced structural rearrangement of cardo-copolybenzoxazole membranes for enhanced gas transport properties", *Journal of Membrane Science*, Vol.397, (2012), P.51-65.

[42] B. Comesaña-Gándara and M. Calle, "Thermally rearranged polybenzoxazoles membranes with biphenyl moieties: Monomer isomeric effect", *Journal of Membrane Science*, Vol.369, (2014), P.369-379.

[43] M. Calle, "Crosslinked thermally rearranged poly(benzoxazole-co-imide) membranes for gas separation", *Macromolecules*, (2013).

[44] M. Calle, "Thermally rearranged (TR) poly(ether-benzoxazole) membranes for gas separation", *Macromolecules*, (2011).

[45] S. H. Han, “Highly gas permeable and microporous polybenzimidazole membrane by thermal rearrangement” *Journal of Membrane Science*, (2010), P.143-151

[46] C. A. Scholes and C. P. Ribeiro, “Thermal rearranged poly(benzoxazole)/polyimide blended membranes for CO2 separation”, *Separation and Purification Technology*, (2014), P.134-140

[47] S. Han, H. Kwon and K. Kim, ”Tuning micro cavities in thermally rearranged polymer membranes for CO2 capture”, *Physical Chemistry*, (2012).

[48] C. Y. Soo and H. J. Jo, “Effect of thechemical structure of various diamines on the gas separation ofthermally rearranged poly(benzoxazole-co-imide) (TR-PBO-co-I) membranes”, *Journal of Membrane Science*, Vol.444, (2013), P.365-377.

[49] C. A. Scholes and C. P. Ribeiro, “Thermal rearranged poly(benzoxazole-co-imide) membranes for CO_2 separation”, *Journal of Membrane Science*, Vol.450, (2014), P.72-80

[50] J. I. Choi and C. H. Jung, “Thermally rearranged (TR) poly(benzoxazole-co-pyrrolone) membranes tuned for high gas permeability and selectivity”, *Journal of Membrane Science*, Vol.349, P.358-368.

[51] Y. S. Do, “Thermally rearranged (TR)poly (benzoxazole-co-amide) membranes for hydrogen separationderived from 3, 3-dihydroxy-4, 4-diamino-biphenyl (HAB), 4, 4-oxydianiline (ODA) and isophthaloyl chloride (IPCl)”, *Journal of Membrane Science*, (2013).

[52] H. Wang, “The evolution of poly(hydroxyamide amic acid) to poly(benzoxazole) via stepwise thermal cyclization: Structural changes and gas transport properties”, *Polymer*, (2011), P.5127-5138.

[53] L. M. Robeson, “The upper bound revisited”, *Journal of Membrane Science*, Vol.320, (2008), P.390-400.

[54] L. M. Robeson, “ Correlation of separation factors versus permeability for polymeric membranes”, *Journal of Membrane Science*, Vol.62, (1991), P.165-185.

[55] D. Q. Vu and W. J. Koros, “Mixed materix membranes using carbon molecular sieves I. Preparation and experimental results”, *Journal of Membrane Science*, Vol.211, (2003), P.311-334.

[56] C. L. Aiken and W. J. Koros, “Effect of structural symmetry on transport properties of polysulfones”, *Macromolecules*, (1992), P.3424-3434.

[57] W.J. Koros and G. K. Fleming, “Polymeric membrane materials for solution-diffusion based permeation separations”, *Progress in Polymer Science*, Vol.13, (1988), P.339-401.

[58] S. Matar, “*Chemistry of Petrochmical Processes,* (2001).

[59] S.H. Choi, “Pilot-scale multistage membrane process for the sepration of CO_2 from LNG-fired flue gas” *Speration and Purification Technology*, (2013), P.170,180.

[60] R. Heck and M. S. Qahtani, O. Garba, “Block copolyimide membrane for pure- and mixed-gas separation”, *Separation and Purification Technology*, (2016), P.183-192.

[61] O. Garba and M. S. Qahtani, “Armoatic block co-polyimide membranes for sour gas feed separations”, *Chemical Engineering Journal*, (2016), P.1020-1030.

[62] Y. C. Xiao and K. Serge, “Mixed gas and pure gas transport properties of copolyimide membrane. *Journal of Applied Polymer Science*, (2013).

[63] A. F. Ismail, ” Penetrant-induced plasticization phenomenon in glassy polymers for gas separation membrane”, *Separation and Purification Technology*, Vol.27, (2002), P.173-194.

[64] Y. Huang and T. C. Merkel, “Pressure ratio and its impact on membrane gas separation processes. *Journal of Membrane Science,* Vol.463, (2014), P.33-40.

[65] W. J. Koros and J.W. Wind, “Natural gas permeation in polyimide membranes”, *Journal of Membrane Science,* Vol.228, (2004), P.227-236.

[66] Z. P. Smith and K. Czenkusch, “Investigation of the chemical and morphological structure of thermally rearranged polymers. *Polymer*, Vol.55, (2014), P.6649-6657.

[67] K. L. Gleason and Z. P. Smith, “Pure-and mixed-gas permeation of CO2 and CH4 in thermally rearrangedpolymersbasedon3,30-dihydroxy-4,40-diamino-biphenyl (HAB) and2,20-bis-(3,4-dicarboxyphenyl)hexafluoropropane dianhydride (6FDA)”, *Journal of Membrane Science*, Vol.475, (2015), P.204-214.

[68] G. L. Tullos and L. J. Mathias, “Unexpected thermal conversion of hydroxy-containing polyimides to polybenzoxazoles”, Polymer, Vol.40, (1999), P.3463-3468.

[69] H. Wang and D. R. Paul, “The effect of purge environment on thermal rearrangement of ortho-functional polyamide and polyimide”, Vol.54, *Polymer*, (2013), P.2324-2334.

[70] Z. P. Smith and G. Hernandez, “Effect of Polymer Structure on Gas Transport Properties of Selected Aromatic Polyimides, Polyamides and TR Polymers”, *Journal of Membrane Science*, Vol.493, (2015), P.766-781.

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